0

(a) Date of Many 11.08.86

Application number: 88307427.0

# Office européen des brevets

EUROPEAN PATENT APPLICATION

1) m. ci. Coaf 4/44 . Coaf 2/50 . C08G 85/12 , C08G 89/88 , C08G 18/16 , C08G 18/22 , G03F 7/00 , C08F 253/00

 Applicant MANUSCOTA MENNIO AND
MANUFACTURING COMPANY St. Paul, Minnesota 66153-3427(US) 34 Center, P.O. Box 33/27

 Date of publication of application ® Prority 28.08.87 US 90894

98.03.88 Busedin 89/10

Designated Contracting States

CH DE ES FRI OB IT, LI NL SE

(9) Inventor Palazzotto, Michael C. c/o Min St. Paul Minnesota 86164-1888(US) Manufacturing Company 2801 Hudaon Road Manage and

Inventor Brown-Wensley, Ketherine A. Invertor DeVos, Robert J. Massesdill Mile St. Paul Marnesota 65144-1688(US) Hanufacturing Company 2501 Hudson Re Winnesota Mining and

St. Paul Istanasota 66144-1686(US) Menufacturing Co. 2581 Hudaen Road

( Representative Buildia, Islan Carl D-9666 Munches 2(DA) C/O Lados & Parry learnerplate 8

Energy induced dual curable compositions.

 An energy polymerizable composition comprises at least one enlyterically-unisabilised monomer, one of polymerizable polymerizable composition comprises at least one epoxy monomer, and a curing agant comprising an organizability polymerizable precursive; and at least one epoxy monomer, and a curing agant comprising an organizability polymerizable polymerizable. compound, and an onlum salt

### METO OF THE MAEMUON

monomer and either polyurethane precursors or an epoxy monomer; and as curing agent a combination of an organometatic compound and an oxidizing agent, and a method therefor in a further aspect, cured example, as protective costings, binders for magnetic media or abrasives, adhesives, and in graphic arts articles comprising the composition of the invention are disclosed. The compositions are useful, for This invertion relates to an energy-polymerizable composition comprising an emylenically-unsaturated

## schground Of The Invention

applications

Tree and & E LOWNER TO ---

. . . . . . . are

# pounds 4 ار . در ا

4.4

solvents. There is an intense effort by law makers, researchers, and industry to promote high and 100% solids formulations to reduce or eliminate the use of such solvents and the attendant costs and environment Various polyment costings and articles are produced in processes involving the use of organic

tal contamination. These processes require a latent catalyst or latent reaction promoter which can be activated in a controlled fashion Thermal curing of polyurethane precursors using reachon promoters such as tin salts and ter-

teryamenes is largern in the art. Curing of polymenzable murtures of polytisocyanates with polytics (referred to as polyurethane precursors) using thermally latent catalysts is known in the art (see for example U.S.

SY Tsay, M. Kushiba. Y.S. Dang, S.L. Cooper J. Appl. Polymer Science, 1985, 30, 847-888, C. Bhuestein Polyme-Plast Technol. Eng. 1981, 17 83-93), and photocuring of polymethane precursors using chazonium polyme-Plast Technol. deadvartages; sensitivity to oxygen, requirement of ultraviolet and or high intensity light, the need for sats, tenteryennes precusors, and organism compounds is also known (see U.S. Patent Nos. 4,544.468. 4.548 945, and EP 28.895. Derwent abstract). All of these methods suffer from one or more of the following Ment Nos 4,521,545, and 4,582,8611 Photocuring of uresture (methacrylates is well known (see T. A. Speckhard, K.K.S. Hwang, S.B. Lin,

Se bussearch eq

THE OFF MANCEDAY · S. we executed . a maters &

Strong spare

... the protor

WITCHIS OF STREET e ganometalic 11 to 10 me

----

· Dungmor.

See of the see

modified resins, loss or disultion of urethane properties, low activity, poor solubility, and poor posities enterey photoactivised not are any methods known that provide for the simultaneous curing of the wethere The dust curing of acrylate-urethane procursor mixtures is known but these curing methods are not

Degre 48-55) 3,705 129) U.S. Putert Nos. 3,709,851, 3,714,008, 3,887,354 and 4,237,242 relate to the use of transition medicorne, such as terrocorne, can be used as a curry accelerator for epoxy mater ats (U.S. Patent No. polymercation of exposede group-containing materials is also known. Among such processes are those in U.S. Present No. 4.008.705, and the online satts of Group VIA elements, perfecularly the suitonium satts, as is dispurped in U.S. Patent No. 3,794,578 and U.S. Patent No. 4,000,274, halomum salts as is disclosed in U.S. Patent No. 3,794,578 and U.S. Patent No. 4,000,274, halomum salts as is disclosed. which we polymenization catalyst is a radiation-sensitive distant salt of a Laws acid (e.g. discontum salts as metal complemes in the reaction between polyepoliides and polykinctional curing additives, but they do not teach the polymenization of eposide group-containing compositions not containing a curing additive. The are disclosed in U.S. Passel Nr. 4,058,400), or a dicarbonyl chaleto compound of a Group MA-VA eleme as a disclosed in U.S. Patent No. 4.085.091. These compositions are limited to ultraviolet radiation for The prior art discloses processes for the polymentation of epoxy materials. It is further known that a

THE PART AND LAND . J. me exposed THE PLOTTED ALTON BE , lace sources of

----

THOOP A SALE

女子者 第二首 The seconds

7. C A SALACT

TOTAL NO. THE ACTIVATION

Puddeng Print

· U.S. OTHERWOOD

THE SOME I

THE PLANE OF THE

THE REPORT OF PULL BY COUNTY

polymercznon Furtermore, the dicarbonyl chalates are mosture sprediction. U.S. Passes No. 4.216.286 teaches the thermal curving of cascincally polymentable compositions using

ones have been described in U.S. Palent Not. 4 158 000. 4 227 978, and 4 623,878. These compositions onum sate and reducing against exclude online sales combined even organic compounds as the curing agent, but do not contain any Redusion dual curable compositions continuing emplanically unsaturated monomers and agony mon

NEGA 109.851 1986 Correct statest 084.915 1983 Devent abstract and 084.615, 1889. Devent casonically expense metands and the curry thereof has been taught tes European Passes Asplication Everyy polymetrizable compositions comprising long sets of organizations complex cations and

> for the photocurry of ethylenically-unsalurated monamers (I) Smess Pul. (1981), H.M. Wagner, M.D. Purbrich, J. Photograph Science, 29, 220-239. The use of certain photocensisters with online sales for interior is unsaturated monomers is jaso woll aroum in the art. This terrimque has Baumann, Wiss Z. Tech Hochech, Laure-Maresburg, 28, 438 (1984); H. R.; and U. Lammer, J. Prais. Chem. 428 (3), 415 (1984); and H. Bauman; Polym J. 22 (4) 313 (April 3, 1985). duplication, copyring, and other imaging systems (see ). Notes in Light for U.S. Paterri Nos. 3,729,313, 3,741,769, 3,688,069, 4,226,232, 4,750,053 an saits have been previously ideactibad for use as phytomisators in addition o Application of Normshiver Halids Photographic processes, Wiley, Naw York Neutral organometalist compounds have been used in comb

# 0 M in &

## Summery of the Invention

restorative and seatern applications, and in unegang applications as prosective and decorative costings, vita, adhesives, binders for curing agains a combination of a organomes Briefly the treased incorporate and eather polyter environment and eather polyter environment of a organization company It is behaved not known in the art that latent, energy induced sim-

curry of ethylenically-uncaturated monograph, in combination with wife monomers, can be achieved by using as curing agains a combination an ornum sail outdoord again

industrial spinant mesta white reducing exempty conducting An industrial process unrovesion is declosed that will reduce the Aggleton processing pintectionly unliving electron beam and in thereby resulting in loses viscosity monomes schultons which are Nove readily available micromers can be used in place of him t capability to parestaining and polymenting such and pagments. . Advantages of commissions of the present invention when unite

increased Rembility in unsugning coatings with specific properties Expanding the scope of cutable monomers to include (1) IN THE SOSICION .

"caspicate paricies (nichard electron bases and " Combination with one of polymethese precuitors and about min. this cump" made the smutures energy-aduced cumu grow is banded to a metal atom ("Base hargeric Chamisty" \* A the to a polymentate product at these to a degree to cause at the re-"organization compaind" mages a charmed track "peoplications curve" means curve by means of each unit

of specyanism groups to seekypesty restitute hydro 1978 D 4971 and polymosyanette, and one or ness messages of the type of year erous to dest as spunds few pueffit a extreme, "march buildens. (polyurethere precurives us aposy operpreses) is 1 🕦 to 🕪 t. "polymentable multira" messe e multira chase to case of ( precurence manus a manus of use of man morror aring at test two cocyangly-earlier hydrogen dame may be to

metal bonds.

the photocuring of Athylenically-unsaturated monomers (G. Smers, Pure G. Appl. Chem. 53, 611.615 Neutral organismetalist compounds have been used in combination with neutral halogenated compounds

1981). H.M. Wagner M.D. Purbrick, J. Photograph Science, 29, 230-235.
The use of certain photosensitizers with colum salts for initiation of polymerization of ethylenically Raumann Wiss Z Fech Hochsch Leuna-Merseburg 28: 439 (1984). H Baumann B Strehmel HJ Timpe Euro J.S. Palent Nos. 3 729 313 .3 741 769. 3,800 006. 4 228 232. 4 250 053 and 4,428,807. H. J. Timpe and H. saits have teen previously described for use as photomitiators in addition-polymerizable compositions (See Application of Nonsilver Halise Photographic processes. Wiley, New York, 1965, pp. 158-193). Aryliodonium Supin alivin Copyring, and other imaging systems used J. Kosar in Light Sensitive Systems. Chemistry and invaluatest monomers is also well known in the art. This technique has found applications in printing. P. 14m J 22 (4) 313 (April 3 1986).

### Summary of the Invention

cuing agent a combination of a organometallic compound and an onlum salt. The compositions are useful as protective and decorative coalings, inks, adhesives, binders for magnetic media or abrasives, in ethy socially unsaturated monomer and either polyurethane precursors or an epoxy monomer, and as Birelly the present invention provides an energy polymerizable composition comprising an

monomers can be achieved by using as curing agent a combination of an organometallic compound and curry of ethylenically-unsaturated monomers, in combination with either polyurethane precursors or epoxy. restorative, and sealant applications, and in imaging applications It is believed not known in the art that latent, energy induced, simultaneous, preferably solventiess dual

an onium salt oxidizing agent Advantages of compositions of the present invention when utilized in 100% reactive coating composi-

Radiati processing particularly utilizing electron beam and photogenerated catalysis has potential An industrial process innovation is disclosed that will reduce minimize, or eliminate the generation of

... for .. Bluesten ... . . . . 4 544 466 TE SOC THE CHINE

ter steel and

D. Milliam Park

•71. 7 BC 14

4 50 30

thereby resulting in lower viscosity monomer solutions which are easier to coat than more viscous obgomer More readily available monomers can be used in place of functionalized oligomers (used in the prior art) capability to: penetrating and polymerizing thick and pigmented coalings

Expanding the scope of curable monomers to include polyisocyanates polyots and epoxides allows increased flexibility in designing coatings with specific properties.

combination with one of polyurethane precursors and epoxy monomers. "dual curing" means the simultaneous energy-induced curing of ethylenically-unsaturated monomers in energy-induced curing means curing by means of electromagnetic radiation (ultraviolet and visible)

Patent No .... . effere account that a

at: 15 Acres 1986 ing if the premane

.. (milite 1

Chambirat Main

F. Dame.

THE STATE AND THE

HIN 00.4 WILL 712, Ser. 1 UCHISUES IN THE STATE OF THE ST

TO SECTION OF THE SECTION Trap and delivery Trap

1. 45. 5 JISI NUSOFT IN

. . .... Salts as Carcinor Salts 25

ier id lidiam fie IND VA SHOTTING

During and the 47. T. B. 4.

> accelerated particles (including electron beam), and thermal (infrared and heat) means. group is bonded to a metal atom ("Basic Inorganic Chamistry", F.A. Cotton, G. Williamson, Wiley, New York, tion to a polymerized product at least to a degree to cause an increase in the viscosity of the composition. "catalytically effective amount" means a quantity sufficient to effect polymerization of the curable composi-"ethylenically unsaturated monomer" means those monomers that polymerize by a tree-radical mechanism. "organometalisc compound" means a chemical substance in which at least one carbon atom of an organic

bearing at least two reocyanate-leactive hydrogen atoms may be substituted for diols and polyola, the ratio and polyrsocyanates, and one or more monomers of the type including diots and polyrisk Compounds 1976 p 497) of rsocyanate groups to rsocyanate-reactive hydrogen atoms is 1.2 to 2.1. "polywethane precursors" means a musture of one or more monomers of the type including disocyanates

"budging ligand" means a ligand that bonds to two or more metals in the presence or absence of metal-(polyurethane precursors or epoxy compounds) is 1 99 to 99 t. "polymerizable mixture" means a mixture where the rabo of (ethylenically-unsaturated compounds)

metal bonds.

. . ... . Aggin der ett

والمناء والمالق . d. . d. . Survey of St

"polysocyanele" means an alighatic or arometic leocyanate having 2 or more leocyanate groups. "oneum sakt" means selfs of casonic compounds such as dezonium, halonium, and hypervalent Group VIA "polyol" means an exphase or aromatic compound containing 2 or more hydroxyl groups; and

# Detailed Disclosure of the Invention

position comprising in the range of 98 to 1 weight percent an ethylenically-unsaturated monomer and 1 to 99 weight percent of either polyurethane precursors or an epoxy monomer and a bicompondul curing agent store specifically, in a preterred embodiment this invention describes an energy polymerizable com-

hardor, the curing agent comprising

1) an organometatic compound having the structure

#### 1.1.4.X

splected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of L' represents none, br 1 to 12 ligands contributing pretections that can be the same or different ligand.

L<sup>2</sup> regresses none, or 1, to 24 ligands that can be the same or different contributing an even number of coverbuling 2 to 12 presections to the valence shell of M. agma-electrons selected from mono-, dir., and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons

(2 represents note, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigms electron each to the valence shall of each M: eats 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups

was the provide that said urganomistatic compounds contains at least one of a metal-metal sigma bond and ave, ver. ver. and vere (consmonly referred to as transiston metals):  $\lfloor 1 \rfloor_{a}$  and with the proviso that  $\lfloor 1 \rfloor \lfloor 2 \rfloor \lfloor 2 \rfloor$  and M are chosen so as to achieve a stable configuration, and

2) an oraum sait owdizing again having the structure if

3.794578, 3.606,006, 4.028,706, 4.058,401, 4.086,055, 4.101,513, 4.216,268, 4.394,403, and 4.623,678, A a an organic casion selected from those described in U.S. Patent Nos. 3,708,288, 3,729,313, 3,741,788. leadily subcord from describen, locarum, and sultonum cations, while more preferably A is selected

K is an amon, the countemps of the orium sets including those in which X-is an organic suitoness or an diplemyhodomum, triphenyteuticimum and phenyterophenyl diphenyteuticinum, and agreemed minister or meetallood, such as CH(\$0)\*, CF(\$0\*, C,H(\$0)\*\*, p-tokusmeetall

AND THE PROPERTY OF THE PROPER rom Groups MA to VA of the Percebt Chart of Elements, Z is a halogen atom, and r is an integer having a total or actual and the metallouis preferently are boron, eluminum, areamony, this areamo, and price income. Preferently, the heliogen, Z., a Chlores or fluorine, illustrative of suitable amons are BY... PF... se a séach X has the formule DZ, wherein D is a matel from Groupe 18 to VIIIB or a metal or metalloid destry, the messer are copper, and, statum, variation, Chromium, mangariess, von

The curving agent can be present in the range of 0 t to 20, preferably 0 t to 10 weight parcent of the age The case of organisms compound to onlive set is in the range of 101 to 1.10 by

egit petroty 61 to 15 by engit The present exertion also promburgace was one of polymerisate precursors and upony monomers comprising the steps ages a process for the polymentation of ethylenically-unashurated

DISCUSSOR OF SER WORK COMPOUND (a) providing a mustice of at least one entremeably-uncatarated monomers and eather poly selflens

> comprising an organometatic compound and an online salt (and all permutations of the (b) adding to said miniture a combination of a catalytically effective amount

alcrementaried components), thereby loining a polymentable mixture, and In a further aspect, there is also provided a method for presenting coaled whices in (c) atoming the minture to polymerics or adding energy to the minture to effect pur

composition of the invention comprising the steps of

in the art, such as bar, hinde, reverse right hausted roll, or span costings, or by dispary and the late, with or without a costing solvent, and (c) applying energy (after evaporation or \_\_ivent, if present) to the afticle to cause (b) costing an energy polymenization musture as described above to the substrate (a) providing a substrate

casing, and extrusion. Applying one-gy to the makine causes polymentation and the invention. The articles can be promited, for example, by techniques such as mooth-In a spit further sepect, there are stip provided shaped articles comprising the  $\mathrm{D}^{\mathrm{d}_{\mathrm{T}}}$ 

polymenzable composition can be used. processing. Solvent, preferably an original solvent in an amount up to a the range of 0 to 50 words percent, most preferably in the rang shaped article. It is not preferred, but it may be describe to add solvered to solubilitie con-8 3 .

compounds in which the sum of the electrons donesed by the lightest and the the valence electrons possessed by the middle for most organisment terrolocular measi-measi bondard, that sum a governed by the "west a total sum of 18, 17, 18, 19, or 20 electrons in the valence shall are include: Time gas rule? This rule states that the most state organizations combin M. 811 (1986) Thus ruly is symmetry tered a sum of 18, 17, 19 and 20 excess; see the term. Therefore, organi There are restrictions on the last num of excitons dended by and ated in the art, howe reculty maked-maked bending are described by formula it in which gr. know that there are excepted to the rule and that or as called the "name created rule". "The effective electron K COM

Que to the mesti-mest interections describing the mest p orbitis to an diger est most everage 1306 (1979) that the district out of the first outside out that is \$400 to. SR or SA SA SA SA SA CASA IN THE VALENCE SHALL PASS nuclear compound, de CVEs, and a letterischer compound, how For compounds described in formula I in which integrated metal-mot reported are also known. Therefore, Or, Ur. C. lat. repounds having a num of 46, 44, 45, 50 CVEs for a translate companied or THE I SHOULD BE COME I have an exceptions to the inscision outling makes and the over ner geometry is seaso to have this did or the CVEs, respectively. Those shift ter, chaier valence electrons (CVR) are counted. A dinuclear car lable for lighted transfers. Harrish, restraint their count electronic around next. tages electricas nute" casa occus, at has been proposed plante motes cucies, MAA MARK or MA S E 

Coracon

Contro (CQ) ModCOn)

Ç

CoffelCOn Bedien

(Code(CO) is Seen Cofo(CO), Octoo to(CO), Sedina

The divisional Group VIA

ine! aid a to umpor and cuting agent are Crisalizated monomer and 1 to mire 3, polymeniation com-

is the saturated compounds and groups and and an armatic compounds each capable of that had be the same or different ligand

unds each donating 2 4 or 6 sigma-electrons amerent contributing an even number of

sitterent each contributing no more than

S.L. J. MedalSI True. 160 from the elements of Periodic Groups

at least tine of a metal-metal sigma bond and as It acrieve a stable configuration, and

4 1\_1 513 4216 288 4 394 403 and 4.623.676 or cations white more preferably A is selected S. Patent Nos. 3 708 296, 3,729 313, 3,741,769

problem and strained or the strain and y thuse in which it is an organic subonate, or p-totuenesurionate p-chloroben-

Gillar variadium chromium mariganese ron Jr. Groups IB to VIIB or a motal or metalloid a haloger alom and ris an integer having a according antimony tin assent and phosstrature of syllable whichs are BF. T. PF. THE BIC Protorably the anions are

the 110 to 10 to adjoin with the 116 by retailable, 0.1.10.10 weight percent of the

coupers comprising the steps with the office of the office morning and either pur welland

EP 0 306 182 AZ

comprising an organometallic compound and an onium salt (and all permutations of the order of mixing the (b) adding to said minture a combination of a catalytically effective amount of a curing egent

alcrementioned components), thereby forming a polymerizable mixture, and

in a further aspect, there is also provided a method for preparing coaled articles containing the cured (c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization

position of the invention comprising the steps of

in the art, such as bar, knife, reverse roll, knurled roll, or spin coatings, or by dipping, spraying, brushing, (b) coating an energy polymerizable mixture as described above to the substrate by methods known

and the like, with or without a coating solvent, and (c) applying energy (after evaporation or when it present) to the article to cause the polymerization

of this coating

casting, and extrusion. Applying energy to the mixture causes polymerization and provides the cured the invention. The articles can be provided, for example, by techniques such as molding, injection molding, in a still further aspect, there are also provided shaped articles comprising the polymerizable musture of

processing. Solvent, preferably an organic solvent in an amount up to 98 weight percent, but preferably in the range of 0 to 90 weight percent, most preferably in the range of 0 to 75 weight percent, of the It is not preferred, but it may be desirable to add solvent to solublize components and aid in

polymerizable composition can be used. tramolecular metal-metal bonding, but sum is governed by the "eighteen electron rule" [see J. Chen the valence electrons possessed by the metal. For most organometalic compounds not involving in-There are restrictions on the total sum of electrons donated by the ligands, L', L', L' of formula I and

a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell are included within the scope of the including intramolecular metal-metal bonding are described by formula t, in which complexed metals having having a sum of 16, 17, 19, and 20 electron, are also known. Therefore, organic netatic compounds not skilled in the art, however, know that there are exceptions to this rule and that organometalisc compo compounds in which the sum of the electrons donated by the ligands and the metal is eighteen. Those 46. 8(1) (1989)]. This rule is sometimes called the "nine orbital rule". "the effective number rule" or the Taxe gas rule. This rule states that the most stable organometalisc compounds wend to be those

unavailable for ligand bonding. Hence, rather than count electrons around each netal separately in a metal que to the metal-metal interactions destabilizing the metal p orbitals to an extent to cause them to be 5305 (1978)] that the departure from the "eighteen electron rule" in these transition metal compounds is that there are exceptions to this electron ounting method and that organometatic complex cluster trinuclear compound. 48 CVEs, and a tetranuclear compound, having tetrahedron, butterfly, cluster, cluster valence electrons (CVE) are counted. A dinuclear compound, is seen to have 34 CVEs. a planar geometry is seen to have 60, 62, or 64 CVEs, respectively. Those stulied in the art, however, know departure from the "eighteen electron rule" can occur, it has been proposed (J. Amer. Chem. Soc. compounds having a sum of 42, 44, 48, 50 CVEs for a timuclear compound and 58 CVEs for a tetranuclear 50: or 58, 60, 62, 64 CVEs in the valence shell respectively, and are included eathin the scope of this formula t in which the complexed metal cluster, MM, MMM, or MARAMM has a total sum of 34, 42, 44, 48, 48, compound are also known. Therefore, dr. tn. or tetranucteur organismessaic compounds are described by For compounds described in formula I in which intramolecular metal-metal bonding exists serious

Bustrative examples of organometalist compounds according to formule I include

[Cofe(CO)2]2

Mnz(CO)10

(CoMo(CO))

Rez(CO):0 4(CO)WQD]

\$00)co Ca.(CO) 2

CoFe(CO)/GePh) CpFe(CO)2 SnPh.

|Cofe(CO)|LSnPh/ (CO, Man SaiPh) CoMo(CO), SnPh

(CO) Min : SoPh:

CON MAPOFTI Cofe(CO); PbPh)

(CO), RoSoPh

Coppedie CpW(CO)1Mo

Cp(CO)1W-MorCO)1Cp Cp(CO)<sub>1</sub>Mo-Re(CO)<sub>5</sub> Cp(CO)1Mo-Mn(CO»

CO(CO), W-Mn(CO)

Cp(CO),Mo-Co(COL CD(CO) W-Re(CO) CD(CO),W-Co(CO)+

Cp(CO),Mo-Fe(CO),Cp (CO), Man-Fe(CO); Cp

CpiCO)<sub>1</sub>W-FeiCO); Cp

CpMo(CO)2PPh12 An (CO) PPT (CO) (PPh)2

(CO), Mn-Re(CO), Mn2(CON (1.10-phenanthroline) Cpfe(CO), J. Si

Rea(CO)(1.10-phenanthroline)

Re2(CO) (2.2 -biquinoline)

Fe<sub>3</sub>(CO)-2 E (CO):

031(CO):2

7.4 . 6.

Rus(CO)+e(Ph;P-CH;CH;-PPh;) Rus(CO): , PPhs

(CO): Fez Ru(CO): 2

CpFe(CO)2CH:Ph CoFe(CO); (COPh) CPM(CO)

CoFe(CO)2(SiPhi)

CP FNCO), b COICO)2FO-FOICOXPPh.JCD

(Maccoperation

Cp(CO)3Mo-Mo(CO)2(PPh3)Cp (Me)SCD)PIMe)

Me is methyl

Ph is phony!

Cp is eta? -cyclopentadienyl

Cp\* is eta\*-pentamethylcyclopentadienyl metracrylates such as methyl acrylate, methyl methacrylate, ethyl acryate, isopropyl methacrylate, mhexyl undergoing addeson polymerization. Such monomers include monor, dir. or poly- acrylates and Sustable compounds containing at least one ethylenically-unsaturated double bond: can be monomers and or obsporeers such as (meth)acrylates, (meth)acrylamides, and vinyl compounds, and are capable of crylate perserythridol triacrylate pentaerythridol tetrascrylate pentaerythritol tetramethiacrylate, sorbitol omethacrylate trimethylologopane tracrylate. 1.2.4-butanethol trimethylacrylate. 1,4-cyclohexanediol disdeenyienegiyool diacrylate. Inethylenegiyool dimathacrylate. 1.3-propanediol diacrylate. 1.3-propanediol acrylate, steavyl acrylate, altyl acrylate, glycerol quacrylate, glycerol triacrylate, ethyleneglycol quacrylate hexacrylate proporyphenyl-dimemylmemene, tris-hydroxyethylisocyanurate trimethacrylate, the bis-acrylates and bis-A wide variety of monomers can be energy polymerized using the curing agent of the invention. bis[1-(2-acryloxy)]-p-ethoxyphenyldimethylmethane. bis(1-(3-acryloxy-2-hydroxy)}-p-

Patent No. 4,642,126, unsaturated amides such as acrylamide methylene "icksic Pair

4 304 705. Mixtures of two or more monomers can be used if desired divinyl succinate, divinyl adipate, drvinyl phthatate, and vinyl azlactories as "scillistical methacrylaminoethyl methacrylate, and vinyl compounds such as styrane. here there methacrylamide 1.6-heiramethylene bra-acrylamide diethylene framina includio

polyisocyanates correspond to the formula heterocyclic privisocyanate, or any combination of such privisorian ales i dual curing systems of the present invention may be any alignatic. Exclosignatic at a The polyisocyanate component of the polyurethane precursors that can be "ure:1  $^{\prime\prime}$ 

#### Q(NCO) =

15 from 4 to 10u carbon atoms and zero to 50 heteroatoms, an aromat in which is an integer 2 to 4, and Q represents an airphasic hydrocarbon divitive of that can be present in Q include non-peroxidic oxygen, sufur non-amino nitrojehydrocarbon radical containing from 8 to 100 carbon atoms and zero aromatic radical containing from 5 to 15 carbon atoms and zero non-phosphino phosphorus carbon atoms, and zero to 50 heteroatoms, a cycloahphatic hydroxin Meter 'a

amethylene disocyanate, 1.12-dodecane disocyanate, cyclobutane-1 3-disocyanate ethylene disocyanate. I.4-ten amerbylene disocyanate i 8-hexamethylene i . compounds with compounds containing two inocyanate-reactive groups 1.5-disocyanate, and the reaction products of four equivalents of the aforementdisocyaliate and mixtures of these isomers, aphenymethane 2.4 - and or - 4.4 disocyanate and mixtures of these isomers, herahydro-1 3-and or -1 4- phenyeane (see German Auslegeschrift No. 1] 22,785. U.S. Patent No. 3,401,190) 24. a -1:4-disocyanate and mixtures of these isomers. 1-isocyanate-3-3.5-bimethyl-5-is 2,4 Yor -4,4 - dichenylmethane disocyanate. 1.3- and 1.4-phenylene disocyanate. Examples of polyisocyanates are as follows

35 In U.S. Patent No. 3,152,182 and in German Otherlegungsschrift Nos. 2 504 F groups of the type described, for example, in British Pasent No. 994 890. in Br norbornane disocyanates according to U.S. Patent No. 3,482,330, pulyisis in 1,157,601 (U.S. Pat. No. 3,277,138), polyisocyanates containing carbodiminite perchlorinated anyl polyrisocyanates of the type described, for example in 848.671, m- and p-socyanatophenyl suphonyl isocyanates according to trisocyanate, polyphenyl polymethylene polyisocyanates described in Britis' described, for example in U.S. Patent No. 3,001,973, in German E According to the present invention, it is also possible for example Application No. 7,102,524, polyisocyanales containing isocya

1,027.794 and German Offenlegungsschrift Nos 1,929.034 and telomerization reactions of the type described for example in U.S. Patent No. 3 of 3,394,184 and 3,844,457. polyisocygneses containing acrylated utell urethane groups of the type described, for example, in Beigian Pil containing ester groups of the type described, for example, in British Pesent Nos. 91 U.S. Pasent No. 3.587.783 and in German Pasent No. 1.231.688, reaction products No. 1,230,778, polyisocyanates containing buret groups of the type described tatty acid esters according to U.S. Palant No. 3,455,883 disocyanates with acetals according to German Palant 1,072,385 and polysisk (4) in الاس 10.0 3.124.605, 3.201.372 and 3.124.605 and in British Palent No. 888.050 الاستان

also possible to use any murtures of the above-mentioned polyisox yeruses production of isocyanates, opeically in solution in one or more of the above-mention Preferred polysocyanates are hesamethylene disocyanate its surgenies It is also possible to use distribution residues having isocyanase groups usia

tolytene dusocyanate and hexamethylene muocyanate, the reaction product of tire (isophorone disocyanate), the tolylene disocymples and their isocyanutes. If and 3 mote of tolylene disocyanate and area crude diphenyl methere disocyanate Suitable compounds containing at least 2 isocyanate-leactive hydrogen bisicyclohexylisocyariate). 1-isocyanato-3.3.5-trimethyl-5-titchy erior

memacrylates of physimylane glycols of molecular weight 200-500, copolymenzable multures of acrylated monomers such at those of U.S. Patent No. 4.652.274, and acrylated oligomers such as those of U.S.

grany! succinate diviny! Edipate diviny! phthalate, and viny! aziactones as disclosed in U.S. Pateril No Patent: No. 4 642 126; unsaturated amides such as ecrylamide, methylene bis-acrylamide, methylene bismethal ylaminoethyl methodrylate, and vinyl compounds such as styrene, divinylbenzene diallyl phthalate. methacrylumide 1.6-hexiomethylene bis-ccrylomide, diethylene triamine tris-acrylamide and beta-

oung systems of the present invention may be any aliphatic, cycloaliphatic, araliphatic, aromatic, or polyisocyanates correspond to the formula 4 304 705. Mixtures of two or more monomers can be used if desired... heterocyclic privisocyanate. The polyisocyanate component of the polyurethane precursors that can be cured or polymerized in the Or . CSTY combination of such polyisocyanates Particularly suitable

Q(NCO), ::

from 4 to 100 carbon atoms and zero to 50 heteroatoms, an aromatic hydrocarbon radical or heterocyclic in which is an integer 2 to 4, and Q represents an alighetic hydrocarbon dir. Iris, or tetra-redical containing hydrocarbon radical confaining from 8 to 100 carbon atoms and zero to 50 heteroatoms. The heteroatoms promatic radical containing from 5 to 15 carbon atoms and zero to 10 heteroatoms or an arabiphabo from 2 to \_\_\_\_\_ carbon atoms, and zero to 50 heterostoms; a cycloaliphatic hydrocarbon radical containing that can be present in Q include non-peroxidic oxygen; sulfur; non-amino nitrogen, halogen, silicon, ord non-phosphino phosphorus

Examples of polyisocyanates are as follows:

one (see Germon Auslegeschrift No. 1.702.785, U.S. Patent No. 3.401.190). 2.4- and 2.6-heizbydrotolylene compounds with compounds contouring two i-ocyanote-resultive groups 1.5-disocythide. 2nd the reaction products of tour equivalents of the storementioned isocythide-containing disocyunde and minures of these isomers, diphenylmethene-2.4 - and/or - 4.4 - disocyanate, naphthylenedisocycnose and mustures of these isomers, hazahydro-1,3-and/or-1,4- phenylene disocycnose, perhydro-1.4-dusocyanate and mixtures of these isomers. 1-isocyanato-3.3.5-trimethyl-5-isocyanatomethyl cyclohexemethylene disocyanate. 1.12-dodecane disocyanate. cyclobutane 1.3-disocyanate. cyclohaidne-1.3ethylene disocyphate. I.4-teti amethylene disocyphate. I.6-hexamethylene disocyphate; timethyl hex 

in U.S. Patent No. 3.152.162 and in German Ottenbagungsschrift Nos. 2.504,400; 2.537.685 and 2.552.350. percharmated anyl palyreacyanates of the type described for example in German Austegeschrift No. 848.671. m. and p-isocycnotophenyt sulphonyl isocyanates occording to U.S. Patent No. 3,454,608. tresocy mate. polyphenyl polymethylene polyreocy anales described in British Patent Nos. 874,430 and 1,157,601 (U.S. Pat. No. 3,277,138), polyisocyonates containing carbodilimide groups of the type described groups of the typo describbod, for example, in British Patent No. 994,880, in Belgich Pat. No. 781,828 and in examinivation reactions of the type described for oxempts in U.S. Patent No. 3,884,108, palyioaxyerieso 1,027,384 and Garman Ottaniagungoschrift Noo. 1,828,034 and 2,004,048, polyisocyandos estillating accordados for cucinque in U.S. Pascott No. 3,001,873, in Germon Patent Nos. 1,022,789, 1,222,087 and norbornone dispocyanutes according to U.S. Patant No. 3,482,330, polysocyanates containing altophanato division from each exception executioning to German Present 1,072,1885 and polymonry analogy constanting polymeric U.S. Potoni Ro. 3,597,763 and in Garman Patoni Ro. 1,231,863, rocation products of the above-marketical consuming occur groups of the type descended, for oscenado, in British Peters Note 1286,474 and 1,072,056, in Nos 3,124 605, 3,201,372 and 3,124 605 and in British Patent No. 889 050, polyreacyandos produced by No. 1,230,778, polyteacycross consciently buriet groups of the type described, for exempts, in U.S. Potent 3,384,164, and 3,844,457, polymocyanisms containing carylated unex groups according to Garman Potant urchizes groupe of the type described, by outmobe, in Bolgus Pasent No. 752,281 or in U.S. Pictert Nos. According to the present invention, it is also possible for example, to use triphenyl mothere-4.4.4. Application No. 7,102,524, polytocypnotes containing tectypnutate groups of the hypo

production of eacytonistic approach in pathetian in one or more of the blood-membraned polyrocal ances it is tony and estors according to U.S. Pricent No. 3,455,533 is a caso possible to use distriction receptorel Burkey provide the provided in the commercial

area boostaps to not but whereing of the openio-worklaned bahirock/paragos tolyteno diasocyanes end houtenethyteno eteatyenato, the rockton product of 1 mol of trimothytal propone leagence one descriptions). The today one descriptions and their lock formittee the mixed least formittee of Prederiod palysocycnetto co houghconytono desocycnoto its reacycnutes and its buriet a.s. bisicycloboxyboscychcib). 1-cocycreso-3.3.5-trimothyl-5-roocycresomothyl Cyclonoscoro

A Miles . . . . . . ale die auc IC MIDELE •

and 3 mais of lightens desocrates and also crues displays messens desocrates compounds contisming it but I backproushousing hydrogon come on to high or be

preferably from about 700 to 2000, for suample, pulyesters, polyethers, polythosiners, polyacetals, groups and above all, compounds having a weight everage molecular weight of from about 500 to 25000. compounds containing hydroxyl groups: perscularly compounds containing from about 2 to 50 hydroxyl in addison to compounds containing amino groups, thick groups or carboxyl groups, are, prelevably, molecular weight compounds, having a weight average molecular weight, generally from about 50 to 50,000 compounds and a less then equivalent quantity of polyisocyanate, of the type known for the production of a, tha preferably from about 2 to 4 hydroxyl groups, or even hydroxyl-containing prepolymers of these least, and polyester amodes, containing at least 2, generally from about 2 to

Saunders and Frisch, interscience Publishers. New York London, and Vol. 1, 1982, pages 32 to 42 and described, for example, in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology"; Hoodhean, Cart. HarraerVerlag, Munich, 1986, for example, on pages 45 to 71. It is, of course, possible to pages 44 to \$4 and Vol. II. 1984, pages 5-8 and 198-198, and in Kunststoff-Handbuch. Vol. VII. Vieweguse muchanes of the above-memboned compounds containing at least two isocyanate-reactive hydrogen some and having a molecular weight of from about 50 to 50,000 for example, mixtures of polyethers and presoves of the above-mentioned compounds used in accordance with the present invention are

consuming compounds with one another (German Ottenlegungsschrift No. 2.706.297). compounds preferably containing hydroxyl groups and generally containing from about 2 to 8, preferably productive weight from about 50 to 400) suitable for use in accordance with the present invention are pe range of from about 50 to 400 Examples of such compounds are emylane glycol, 12- and 1.3compounds containing at least two isocyaniste-reactive hydrogen atoms and having a molecular weight in propyress glycol. 1.4 and 2.3-budy-ene glycol. 1.5-pentane diol. 1.6-herane diol. 1.8-octane diol. neopentyl from about 2 to 4 docyanater reactive hydrogen atoms. It is also possible to use mixtures of different democrisme givest, higher polypropylene glycots, disturylene glycot, higher polybutylene glycots, 4.4. 3.723.362), giycardi, ermethylolpropane, 1.2.6-hexanetrol, trimethylolethane, pentaerythritol, quintiol manglycol. 1.4-bat-hydroxy-nethyl cyclonexare. 2-methyl-13-propane diol. albromobulene diol (U.S. Patent No nagot, sorbaci, duamyteme głycot, trednyteme głycot, tetraethyteme głycot, nigher potyethyteme głycots. in some cases, it is particularly advantageous to combine low-melting and high-melting polyhydroxyl molecular weight compounds containing at least two isocyanate-reactive hydrogen atoms

and hydrony lustones ("formose") or the polyhydric alcohols obtained therefrom by reduction ("formitol") 2,539,064, 2,714,064, 2,714,104, 2,721,186, 2,738,154 and 2,738,512) Solutions of polysocyanate polyadwhich we formed in the autocondensisson of formaldehyde hydrate in the presence of metal compounds as polyhydrasodicarbonamides, in low molecular weight polyhydric alcohols may also be used as the polyol tages products, particularly schapors of polyurethane ureas containing ionic groups and or solutions of Other polydis suitable for the purposes of the present invention are the mixtures of hydroxy aldehydes drawy diphenyl propiers and dihydroxy methyl hydroquinons. lysts and compounds capable of enedtol formation as co-catalysts (German-Offenlegungsschrift Nos

in the present envertion, and are obvious to those studed in the art of polyurethane science and technology Example compounds that can be cured or polymerized in the qual systems by the curing agents of this Many other compounds containing isocytate-reactive hydrogen aloms and polyisocytanates are useful paest in accordance with the present invention (German Ottonlegungsschrift No. 2,638,759) using the littler in a catalysically effective amount, are those known to undergo cationic tion and exclude 1.2-, 1.3-, and 1,4-cyclic letters (also designated as 1.2-, 1.3-, and 1,4-sportdes)

in "Reig-Opening Polyments: "Ire". Vol. 2, by Frisch and Reegan, Marcel Dekter, Inc. (1969). Suriable 12-The 1.2-cyclic esters are profurred. Parecularly useful are the apphase, cyclosephase, and glycidyl ether type 1,2-spouldes such as propylene cyclic eleans are the expromeric and polymetric types of epoxides. They can be airphatic cycloairphatic polypusadone. 1.4 outanediol digitadyl ether, polyglycidyl ether of phenoitormaidenyde resole cr novolak unde, apichiorchydan, afyrane omde, ymylcyciohemene omde, ymylcyciohemene domde, glycidol, buladiene 3,4-eposycyclohesenecerbosylete. use. glycosyl methocrylese, digrycosyl ethar of bisphenol A, cycloheuseneoxide, 3,4-epoxycycloheusenethyl-The cyclic effects which can be polymerized in accordance with this invention include those described recerbonyles. Diskâ A-epony-4-methylcyclohenylmethyljadipsia dicyclopentadione dioxide eponidized searcyclic and well typically have an epoxy equivalency of from 1 to 6, preferably 1 to 3

seen, secorcards diglycubys either and epoxy secones, e.g., dimethylisticianes having cycloaliphatic epoxide or glycidyl ether groups A wide variety of commercial epoxy resints are available and listed in "Handbook of Epoxy Resins" by

> Bruns, John Wiley & Sons, New York (1988). Representative of the: 1.3- and 1.4-cyclic effers which can be Lee and Neville: McGraw Hill Book Company. New York (1987) and in "Epoxy Resin Technology" by P. F. accordance with this invention are oxistane. 3.3-bis(chloromethy))oxistane - ark

ochylene oxide, phenyl glycidyl ether, 1,2-butane oxide, laglycidyl ether of bisphenol A (e.g., "Epon 82f tetrahydrofuran, styrene oxide, cyclohexeneoxide, vmylcyclohexene oxide, głycidol, głycidyl methacrylek 80"), 1.4-butanediol diglycidyl ether (e.g. Araldas RD-2), polyglycidyl ether ot phenostormaidenyde novo сусю́нежалесаrboxylate (е.д. "ERL-4201"), bisi3,4-ерожу-6-тевтуюсусюлежуютевтупафраве (е.д. "ER tetrahy droituran. diguide (e.g., "ERL-4269"), eposidized polybutadiene (e.g., "Osiron 2001"), secon eposy (e.g., "Syl-Ku 4288"), alighabic epoxy modified with polypropylene glycol (e.g. "ERL-4050" and "ERL-4052"), dependent ycyclohexanecarboxylate (e.g., "ERL-4221"), 3,4-spoxy-6-methylcyclohexylmethyl 3,4-spoxy-6-methy and "DER 331"), unryicyclohexene doxide (e.g. "ERL-4206), 3,4-epoxycyclohexylmethyl-3,4-epo (e.g., "DER-431", "Epi-Rez 521" and "DER-438"), resorcinol diglycidyl ether (e.g., "Ropoule"), pollyulir dieposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate eposide (e.g., "Epocryl (L-14"), urethane modified eposide (e.g., "DER 736"), polyacrylate (e.g., "DER 736 mustures thereof with co-curatives, curing agents, or hardeners which also are eet h Neville and Bruins, supra). Representative of the co-curatives of hardeners which q "Oxigs88"), polyfunctional flexible epoxides (e.g., "Flexibilizer 151"), and mixtures thereof as eei arhydrides such as nadic mediyi arhydride. cycloperlaneseracarboxylic diarhydrid In particular, cyclic ethers which are readily available include propylene oxide, oxetane, epichlorohydiri

dride, cis-1.2-cyclohexanedicarboxylic anhydride; and mixtures thereof curing agents useful in the invention have the formula As noted above, the organometalisc compounds useful in combination with onum satts to provide

[ 'L' 'L' K

methanol, a ketone, eig., methyl ethyl ketone, an ester, eig., amyl acetate, a naiocatbon o is propared) bearing the unstabilitated group is soluble in a reaction medium, such as an accir toroemyteine, an alkane, e.g., decalin, an aromatic hydrocarbon, e.g., anisote, an adher e.g., tell'at group which has accessible prejections regardless of the total molecular weight of the complicing accessible unsaturated group, i.e. an emylenic. . E. la.E. . group acetylenic . Cel.C. group of at group (including aromatic group) is sufficiently crose to a metal atom to form a process of etc. or that the compound is divisible into very line particles of high surface area so that the u unsaturated group and the metal atom. By polymeric compound, is meant, as explained tele-Ligands L'-to L' are well known in the art of transition metal organizmetalist compounds Ligand L' of general formula it is provided by any monomeric or polymeric compound rait is meant that the compound for preclusor compound from which the accession con-

from nitrogen subtrance-perculaic augen phosphorous, arsenic, seenium boton, ansimon, sucon, germanum, and on, such as, for example, emylene, acetylene propylene methylacc 100 carbon atoms, preferably having less than 60 carbon atoms, and from zero to 10 netero atom. ligand can be a group on a polymeric chain butene, 2-butene, diacetylene, butadiene, 1,2-dimetriyjacetylene, cyckoutene, pentg octone. 3.4-dimethyl-3-hevene, and 1-decene, eta2-allýr eta2-pentenyl norbonadoen ené, cyclohezene. 1.3-cyclohezadiene. cyclopentadiene. 1 4-cyclonezadiene. cyt Bustrative of ligand L' are the linear and cyclic ethylenic and acetylenic compounds.havid 45.

memane, paracyclophane, 1.4-dipnen, ibutane, eta) pyrrote, eta) micphene, eta) butan. Dyridin heterocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms and up to 10 heter etal-cycloneplatiene, etal-cyclopotasetteene, and substituted leliurium, sucon, germanium, and lin, such as, for example, exa<sup>‡</sup>-cyclopeniadienyi bentene, me selected from nitrogen, subur, noi-peroxidic oxygen, phosphorous, arsenic, selenium, boron ar suitable aromabic compounds can be found by consulting any of many characal handbooks navamethytbonzone, fluorene, naphthalene, anthracene, chrysene, öyrene, eta'- cycloheptatrienyi ir silabanzana asabanzana sibbabanzana. 2.4.6-triphunyiphosphabunzana alai-salanophuna ditu mapicoline, quinaldine, benzopyran (hiochrome, benzosazine inoque, acridine, carbazole napina stali teliurophena, phanotilutana, selenalitirana, phenitating phanotilutana lurazine, eta\*-methylcyclopentadienyl: eta\*-pentamethylcyclopentadienyl: and 1-phenylburaden/si and unsubstituted

polystyrene, polyistyrene-co-butaciene), polyistyrene-co-mainyl methaciylate), noryiaicha-methi polyvinyicarbaccia and polymethylphenylsiloxana, the cycloperitablena group in polytrinyicyclores As mentioned before the ligand can be a limit of a polyment for example the pheny.

Bruns, John Waley & Sons, New York (1988) Representative of the 1.3- and 1.4-cyclic ethers which can be Lee and Neville. McGraw Hill Book Company. New York (1987) and in "Epoxy Resin Technology" by P. F. polymenzed in accordance with this invention are oxistane.

сусіольналесагрозунава (в 9. "ERL-4201"), bisi3.4-ероку-8-methylcyclohexylmethyladipata (в 9. "ERLand "DER 331"); vinyxyclohexene diaxide (e.g.; "ERL-4208), 3.4-epaxycyclohexylmethyl-3.4-epax ochylene oxide, phenyl glycidyl ether, 1,2-bulane oxide, diglycidyl ether ol bisphenol A (e.g., "Epon 828" seganydroburan, styrene oxide, cyclohexeneoxide, vinylcyclohexene oxide, glycidol, glycidyl methacrylate, dioxide (e.g. "ERL-4268"), epoxidized polybutadiene (e.g. "Oxiron 2001"), silicon epoxy (e.g. "Syl-Kem 4289°), alighabic epoxy modified with polypropylene glycolile g . "ERL-4050" and "ERL-4052"), dipentene ycyciohexanecarboxylate (e.g. "ERL-4221"). 3.4-epoxy-8-methylcyclohexylmethyl 3.4-epoxy-8-methyl-90"), 1.4-butanediol diglycidyl ether (e.g. Araldite RD-2), polyglycidyl either of phenoitormaldehyde novolak (e.g., "DER-431", "Epi-Rez 521" and "DER-436"), resorcinol diglycidyl ether (e.g., "Kopaxis"), polyglycol annydrides such as nadic methyl annydride, cyclopentanetetracarboxylic diannydride, pyrometibo anny-Neville and Bruns supra). Representative of the co-curatives of hardeners which can be used are acid mustures thereof with co-curatives, curing agents, or hardeners which also are well known (see Lee and deposide (e.g., \*DER 736\*), polyacrylate eposide (e.g., \*Epocryl U-14\*), urethane modified eposide (e.g., "QX3588"), polytunotonal flexible epoxides (e.g. "Flexibilizer 151"), and mixtures thereof as well as in particular, cyclic ethers which are readily available include propylene oxide, oxetane, epichlorohydrin.

gride, cis-1,2-cyclohexanedicarboxylic anhydride, and mixtures thereof As noted above, the organometalic compounds useful in combination with onlum saits to provide the

curing agents useful in the invention have the formula

T L

The annious user manager on

المعاملات أن دفاساد...)، مدر or negani invention are a the involvagent atoms

ANDRIBLIAND B OF STORES

... et of phyemes and

armed the hydrogen .. Luise possible to

· V. VII VIOLET

and the statement and

ان مضاربراین، - ب press of those

turi tu 25000 e, at and 2 to in ha olais-Su madricays , i elerial i,

To Moundy

recting polyhydroxy!

JULY JULY PAIGN NG , or portellisione grycols

taory tolitor solitory man-

اوالمعتندهم سن مداوا سن :

E I Duly Scurpanate polyad-

o St moter compounds as

Jinerwywigsschrift Nos Cy reduction ("formatol")

IL US OF DYCHONY ALCOHYOMS

... tuly ene glycois . 4.4

Ligand L. of general formula I is provided by any monomeric or polymeric compound having an accessible unsaturated group, 18, an emylenic. - £ = £ - group, acetylenic, -C=C- group, or aromatic is prepared) bearing the unsaturated group is soluble in a reaction medium, such as an alcohol. e.g. group which has accessible prejections regardless of the total molecular weight of the compound. By iproethylene, an alkane, e.g., decain, an aromatic hydrocarbon, e.g., anisole, an ether, e.g., tetrahydrofuran medianol, a kelone, e.g.; mediyi etiyi kelone, an ester, e.g., amyi acelale; a halocarbon, e.g., trichunsaturated group and the metal atom. By polymeric compound, is meant, as explained below, that the group (including aromatic group) is sufficiently cluse to a metal atom to form a pi-bond between that est, or that the compound is divisible into very tine particles of high surface area so that the unsaturated Ligands L' to L<sup>1</sup> are well known in the art of transition metal organicmetallic compounds. it is meant that the compound (or precursor compound from which the accessible compound

from nitrogen suitur, non-peroxidic oxygen phosphorous, arsenic, selenium, boron, antimony, tellurium, 100 carbon atoms, preferably having less than 60 carbon atoms, and from zero to 10 hetero atoms selected agand can be a group on a polymeric chain butene 2:butene diacetylene butadiene 12-dimemylacetylene cýclobutene pentene cyclopentene haxsucon germanium, and tini such as, for example, ethylene, acetylene, propytene, methylacetylene, 1eta\*-cycloneptatriene eta\*-cycloocialetraene and substituted and unsubstituted carbocyclic octane 3 4-dimethyl-3-hexene, and 1-decene, eta<sup>1</sup>-allyl, eta<sup>1</sup>-pentenyl, norbornadiene, eta<sup>1</sup>-cyclohauadienyl, ene. Cyclohexene. 1,3-cyclohexadiene. cyclopentadiene. 1,4-cyclonexadiene. cycloheptene. 1-octene 4memane paracyclophane, 1,4-dipnenyibulane eta<sup>s</sup>-pyrrole, eta<sup>s</sup>-thiophene, eta<sup>s</sup>-huran, pyridine, gamselected from nitrogen, sulfur, non-peraxidic oxygen, phosphorous, arsenic, selenium, boron, aritmony, mapicoline, quinaldine, bencopyran, thiochrome, benzoiazine, indole, acridine, carbazole, triphenylene, tellurium sulcon germanium, and tin, such as, for example, eta<sup>3</sup>-cyclopentadienyl, benzene, masilylene neserocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms and up to 10 hetero atoms suppenzene arsabenzene stibabenzene. 2.4,6-triphunyiphosphabenzene eta<sup>3</sup>-selenophane, dibenzostannavamethylbenzene, fluorene, naphshalene, antivacene, chrysene, pyrene, eta? - cycloheptatrienyl, triphenylsuracia arcmatic compounds can be found by consulting any of many chamical handbooks Luazine eta: -metrylcyclopentadienyl, eta: -pentametrylcyclopentadienyl, and, 1-phenyltorabenzene. Other nacuma etal-taeurophana, phanoduarsina, salonandrana, phanolaphosphina, phanaisszina, phanaist-Blustrative of legand L' are the linear and cyclic ethylenic and acetylenic compounds having less than

יישור ביישבישל בשווילויל the confidences of max ing to letter and technology. t . ... sucratiales are úseful n. 4. 2 638 551 atu ter used as the polytil , Lus and or southons of

. J. and 1 4-bitaidesi

فالمنازع فالمراز مثاري

1969, SUIBLIE 12.

and fair to the sample of the

and the second second

. In profesal at 1 % 3

e le gallaci Eulaciele

polyvinyicarbazule, and polymethylphenylisilozane, the cyclopentadiene group in polylvinylicyclopentadiene).

porystyrene poryistyrene-co-butadiene). poryistyrene-co-methyl methacrytate), polyialpha-methylstyrene),

As mentioned before the ligand can be a unit of a polymer, for example, the phenyl group in

סטים ייינים שנייים in the state of th

And of borners, and

AND A SECURITY OF THE ASSESSMENT OF THE PARTY OF THE PART

to brail come. No

Le lieb as hasins to

the pyridine group in polytrenyloyindine), etc. Polymers having a weight average molecular weight up to the pyridine group in polytrenyloyindine), etc. Polymers having a weight average molecular weight up to 500 percent of the unsaturated or aromatic groups (200,000 or more can be used it is preferable that 5 to 50 percent of the unsaturated or aromatic groups

ILCDUSTULOR completed with metalist Cabons present in the polymer be completed with metalist Cabons in the polymer be completed by groups that do not interfere with the extern that completing with the Each ligand it can be substituted by groups that do not interfere with the extern state only interfere as substituting groups, all of which preferably have less than 30 the metal atom or which do not reduce the substituting groups, all of which preferably have less than 30 the metal atom or which to 10 heaters atoms selected from introgen, suitur, non-peroxicic oxygen, prosphorus, action atoms and up to 10 heaters atoms selected from introgen, suitur, non-peroxicic oxygen, prosphorus, areas, and up to 10 heaters atoms selected from introgen, suitur, non-peroxicic oxygen, prosphorus, as metalist, activities, eatificities, and prenoxy, teathers, and athyrist as metalist, activities, eatificities, and prenoxy, teathers, and prenoxy, processory, and p

percendic oxygen, phosphorous, areenic, selenium, artemony, and tellunum, whereupon addition to the metal containing up to about 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, noncompounds or groups are carbon monoxide, carbon suitide, carbon selenide, carbon telluride, alcohols such as educated, butanted, and phenot; nitrosomum (i.e., NO.), compounds of Group VA elements such as metal. M. a. 4-, 5-; or 8-membered saturated or unsaturated ning; Examples of suitable monodentate appm, tollowing loss of zero, one, or two hydrogens, the polydentate compount, referably forming with the dispocyanupropare, and hydrodotroyrrazolyborate; the hydroxycarboxylic acids such as glycolic acid, lactic such as enunymethylcarbene, dithomethoxycarbene, alkyldenes such as methylidene, ethylidene; suitable ene, trahenylanbine, trabulylahosphite, isonatiles such as phenylaonatile, butylisonitrile; carbene groups polydentate compounds or groups include 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane. amezona, phosphine, trimediylariine, trimediylphosphine, triphenylariine, triphenylphosphine, triphenylar acid, sakcylic acid. polyhydric phenola such as catechol and 2.2 dithydroxybiphenyl; hydroxyamines such dicarbonylic (faminies as outsamide, biurel; diketones such as 2.4-pentanedione; hydroxykulones such as 2confuoromethyl)-1.2-distrotene, aminocarbonylic acids such as alarune, glycine and o-immobenzoic acid. Each 1 and L<sup>2</sup> in formula 1 is provided by monodentate and polydentate compounds preferably CM\* . BCM\* , F\* , OM\* , CI\* , Br\* , I\* , and M\* and the organic groups such as, for example, acetoxy. hydroxyacetophenone, alpha-hydroxyoximes such as salicytaldoxime; ketoximes such as benzil oxime; and sancyddeniorarbemies: kandhees such as ethyl kanthaes, phenyl kanthale; the ditholenes such as bisethanolamine, propandiamine, and 2-aminophenol; dithiocarbamates such as diethyldithiocarbamate. mylony, benzoylony, etc. As mentioned before, the ligand can be a unit of a polymer, for example the ses such as dimethylighoxime. Other suitable groups are the inorganic groups such as, for example, emylenediamine. propylenediamine. diethylenemamine.

amo group in polytethylemeanine); the phosphino group in polyte-vinylphenylphenylphosphine) the cabbright and group in polytethylecardic acid); and the isomitrie group in polyte-vinylphenylaboritrie).

Sustable ligands L3 in formula 1 include any group having in its structure an atom with an inchared discrete. Sustable groups can contain any number of carbon atoms and heleso atoms but preferably contain asserting and the stronges. Buttur, oxygen, prosphorus, asserting a substance at the property of the stronges and the substance of such groups are asserting and preferably, eating, propyl, heavyl, dodecyl, phenyl, toyl, etc.; unasturated hydrocarba-pouga such as well, etc.'-with, etc.'-phenyl, etc.'-phenyl, the hydrocarbyl derivatives of a Group techniques such as well, etc.'-with, etc.'-phenyl, etc.'-phenyl, the hydrocarbyl derivatives of a Group techniques auch as transfiringermyl, sub-thenyl-stancyl, transfiritallyl, and triphenylesid, etc., and organic triphenylesid, acid, acid, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidocoyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidocoyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidocoyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidocoyl, proponyl, acidocoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, orange such as tomyl, acidocoyl, proponyl, acidocoyl, benzoyl, benzoyl, toluenesuitonyl, oxalyl, malonyl, oxalyl, malonyl, oxalyl, malonyl, oxalyl, malonyl, oxalyl, acidocoyl, proponyl, acidocoyl, benzoyl, benzoyl, toluenesuitonyl, oxalyl, acidocoyl, proponyl, acidocoyl, benzoyl, benzoyl, toluenesuitonyl, oxalyl, acidocoyl, proponyl, acidocoyl, benzoyl, benzoyl, toluenesuitonyl, oxalyl, acidocoyl, acidocoy

proups such as tomps, surpsy, property, and the structure two, three, or four unshared electrons, with the patients at 1 s any group having in its structure two, three, or four unshared electrons with the Aleco electron is shared per metal. M. Examples of such groups are CH<sub>2</sub>, SiMe<sub>2</sub>, SiPh<sub>2</sub>, Aleco electron is shared per metal. M. Examples of such groups are CH<sub>2</sub>, SiMe<sub>2</sub>, SiPh<sub>2</sub>, Aleco electron is shared per metal. M. Examples of such groups are CH<sub>2</sub>, SiMe<sub>2</sub>, SiPh<sub>2</sub>, Aleco electron is shared per metal.

provide that day one section is that by provide the provide that the section is that by the provide that the provide the provide the provide that the provide the pro

go can be any element from Fe, Ru, Os, Co, Rh, Y, Is, Pd and Pt.

Zi, ett. V, 8tb. Ts, Cr. Ms, W; Ms, Tc, Re, Fe, Ru, Os, Co, Rh, Y, Is, Pd and Pt.

Is general: exhibitor-induced polymentation of ethylenically unsettated monoment and one of polymentation of ethylenically unsettated monomentatic compound the pecurisists and epony empiricals with items curing agents comprising an organometatic compositions, and an online sait can be carried out at room temperature for the majority of energy curable compositions.

although low temperature (e.g., 1.0°C) or elevated temperature (e.g., 1.0°C) preferative (e.g., 1.0°C) or elevated temperature (e.g., 1.0°C) or elevated temperature or to accelerate the polymeration or to accelerate the polymeration and amount of catalyst will vary and be dependent respectively. Temperature of polymeration and amount of catalyst will be polymerated or cured produce particular curable composition used and the desired application of the polymeration should be sufficient to effect polymerations. Such amount of curing agent to be used in this invention amount under the desired use conditions. Such polymeratable mixtures (i.e., a catalystically effective amount) under the desired use conditions of the catalystically effective amount percent, and preferably 0.1 to 10.0 weight polymeratly will be in the range of about 0.1 to 20 weight percent, and preferably 0.1 to 10.0 weight percent.

generally will be in the familiar or provided in the weight of curable composition based on the weight of curable composition while not enstring to be bound by theory, we propose that when specified organometalic composition while not enstring to be bound by theory, we propose that when specified organometals unestimate and whyli monomers it is believed produced which can affect the curing of epocades unestimate and whyli monomers it is believed produced which can affect the curing of epocades unestimate compounds such as [CpFecCO::1. transition metal-transition metal-transition metal-to some organometatic compounds such as [CpFecCO::1. transition metal-transition metal-to produced by some organometatic compounds such as [CpFecCO::1. transition "Organometatic Photococopic data provides such evidence (0 Heckeberg, A Wolcicki Ir (CO): and involves the abstraction of A Wolcicki Ir (CO): and involves the spectospic data provides such evidence (0 Heckeberg, A Wolcicki Ir (CO): a self-to-defense organometal-to-defense of the spectospic organometal-to-defense of the spectospic data provides such evidence (0 Heckeberg, A Wolcicki Ir (CO): and to-defense organometal-to-defense of the spectospic data provides such evidence (0 Heckeberg, A Wolcicki Ir (CO): a provided to the production of the organometal-to-defense and two free ration of the organometal-country or the segma bond to rate or defense organometal-country the production of two organometal-country and two free ration can ultimately lead to the production of two organometal-country and two free rations can ultimately lead to the production of two organometal-country and two free rations and two free rations.

can occur. Such processes, however, occur in such a manner or to such an extent that catalytic species and inhabitor are still produced so as to effect curing of the composition. Softwents, preferably organic can be used to assist in dissolution of the curing agent in the Softwents, preferably organic can be used to assist in dissolution of the curing agent in the constitution months. In some analysis of the polyurethane precursors or epoxy monomers, and as a cross-station control monomer, and ether polyurethane precursors or epoxy monomers, and as a cross-station control con

support such as since, auminitia, usign, which are radiation-sensitive, i.e. the compositions of the invention which are radiation-sensitive, i.e. the compositions of the invention which are radiation-sensitive, i.e. and an online said either polyurethane precursors or epoxy monoring agent a combination of an organometaliac compound of Formula I and an online said agent a combination of an organometaliac compound of Formula I and an online said agent action beautiful to appear radiation and radiation sources emitting action action and visible region of the spectrum (e.g., about 2010 to 800 nm) can be used subjected and visible region of the spectrum (e.g., about 2010 to subjected lamps). In a carbon arcs, tungsten lamps are radiation include marcury vapor discharge lamps, about polymerization is dependent unsaturated monomer. The organometalistic compound and onlum said the path the identity and concentrations of the organometalistic compound and onlum said the path the identity and concentrations of the organometalistic compound and amount and animals.

Thermal polymenzation using direct heating or intered electromagnetic (\$ \$ 3.5 thermal polymenzation using direct heating or interest and either polymentarie process the used to cure environmentally-instabilization.

as monomers according to he teachings of this invention.

It is within the scope of this invention to nichide two-stage polymerization (curing it is within the scope of this invention to nichide two-stage polymerization (curing agent by virabilishing the curable compositions and subsequently thermally curing curing agent by virabilishing the curable compositions and teaching the virabilishin temperature therefore the curing with an advantage in the railing tower than those required for the direct thermal curing, with an advantage in the railing tower than those required for the direct thermal curing, with an advantage in the railing tower than those required for the direct thermal curing.

and advantageous manner

Adjuvants such as solvents, pigments, abritaive granules, stabilizers, light stabilizers of adjuvants such as solvents, pigments, colorants, inan blees, binders, blowing agents. Items agents, colorants, inan blees, binders, binders, binders, binders, binders, binders, and other additives as troown to those suited in the articles surfactions of this invention. These can be added in an amount effective for their invention. Compositions of this invention are useful for costings, loams, rulaged articles, and moist compositions of this invention are useful for costings.

ar smalk groups

art a pre common and ac-THE PART WITH THE PARTY OF articles such as memori . ... at it girups such as THE PROPERTY OF A PARTY OF A PART . The artist groups such John Branch Branch amony: and aminyi AL . "IB-M MESS MAIN 30 surondsoud setter. more guirante . If me igand with

CODENTA NADRITO

Cons of Suitable monodental minate compounds preferably nem rudono oblytidano, sutabio trulty sonere carbare groups HUNENYONOSONING, INChenyler-Frendución addition to the meta \*\*: from natrogen suffut non-SHOULD VA COMMENTS SUCH AS 1 2-bisidighenylaramojethane artion totale de alcohols such CHORT WELLER A LIBORO -citeratory forming with the

allo the administrate such as bisto example to Anapper explanation for the united to and rigues such as for example OF THE PHYDROXYN LIDNES SUCH AS 2bris and oranadoanacid and SINT AS GONNYOUNGCARDS ... LACK-ON I THY DECK HARMAN SUCH a unullinenyteonetite) - Filsenhoomenyomosphine. Se unies such as henze ocene and TE SUCH AS DIVICONE ACID. NICHE

" the an atom well an employed THE ANDY: Openizatives of a Group tine of unservised hydrocar signative and organic and organic - myesuthmy water majoryt o t sumples of such groups are atums but presentably contain Suito onygen proapholus

Julie aus CH. Salto. . . . i just to one trons ; writte the

Title Sunt as for example Ti the and one of polywer municipalitic computed Liable Compositions

> particular curable composition used and the desired application of the polymenzed or cured product. The amount of curing agent to be used in this invention should be sufficient to effect polymerization of the respectively. Temperature of polymenzation and amount of catalyst will vary and be dependent on the amough low temperature (e.g., 10°C) or elevated temperature (e.g., 30 to 200°C preferably 50 to polymerizable minures (i.e., a catalytically-effective amount) under the desired use conditions. Such amount 150°C) can be used to subdue the exotherm of polymerication or to accelerate the polymerization generally will be in the range of about 0.1 to 20 weight percent, and preferably 0.1 to 10.0 weight percent.

are irradiated in the presence of suitable oxidizing agents such as onlum salts, intermediate compounds are based on the weight of curable composition transition metal-transition metal or metal-L<sup>3</sup> sigma bond cleaves homolytically upon photolysis. Evidence for produced which can affect the curing of epoxides, urethanes, and vinyl monomers, it is believed that the White not wishing to be bound by theory, we propose that when specified organometalisc compounds

Winghton, "Organometalisc Photochemistry," Academic Press, NY (1979), Chapters 2 and 8, particularly p thus nomolytic cleavage is provided for some organometallic compounds such as [CpFe(CO)] and Mng-Acts 1987, 44 L63, R. G. Severson, A. Worcicki J. Organomet. Chem. 1978, 157, 173). The productist of this bond homolysis then react with the oxidizing agent. By this process, the catalytic species for the (CO): a and involves the abstraction of CI from CCLL subsequent to photolysis (G. Geoffrey and M. polymerization of either the polyurethane precursors or epoxy monomers is derived from the organometalic can ultimately lead to the production of two organometalisc-derived species and two free radical instators. It rated monomers is derived from the oxidizing agent. In the limit, cleavage of the sigma bond by one photon compound, and, simultaneously the free radical initiator for the polymerization of the ethylenically unsaft-138) in other cases, spectroscopic data provides such evidence (O. Hackelberg, A. Wojcicki knorg should be noted that competing or secondary photo processes, such as dissociation of a carbonyl ligand. can occur. Such processes, however, occur in such a manner or to such an extent that the effective

catalytic species and initiator are still produced so as to effect curing of the composition. unstable and monomer, and either polyurethane precursors or epoxy monomers; and as a processing aid. yethane (glyme) in some applications, it may be advantageous to adsorb the curing agent onto an inert metrylene chloride, nitromethane, methyl formate, ecetonitrile; gamma-bulyrolactone, and 1,2-dimetrox-Representative solvents include acetorie, methyl ethyl ketorie, cyclopentarione, methyl celtosolve acetate. Solvents, preferably organic can be used to assist in dissolution of the curing agent in the ethylenically-

ethylenically unsaturated monomers and either polyurethane precursors or epoxy monomers and as curing support such as since, alumine, clays, etc., as desembed in U.S. Patent No. 4,677,137 ultraviolet and visible region of the spectrum (e.g., about 201 to 800 nm) can be used. Suitable sources of unsaturated monomer: polyuretherie precursors, and epoxy monomers, the truckness of the exposed the identity and concentrations of the organometalist compound and onlum salt, the particular ethylenically surright, etc. The required amount of exposure to effect polymenzation is dependent upon such factors as radiation include mercury vapor discharge lamps, carbon arcs, lungsten lamps, xenon lar-ps, lasers, source of radiation including electron beam radiation and radiation sources emitting active radiation in the agent a combination of an organometalist compound of Formula I and an online salt of Formula II, any eserual type of substrate, miensity of the radiation source and amount of heat associated with the For those compositions of the invention which are radiation-sensitive, i.e., the compositions containing

can be used to cure ethylenically-unsaturated monomers and either polyurethane pre-ursors or ecoxy Thermal polymenzation using direct heating or infrared electromagnetic radiation, as is known in the art.

quent heat-curing. These activated precursors may normally be cured at temperatures which are substanprecursor so obtained, the irrediation temperature being below the temperature employed for the subsecuring agent by eradiating the curable compositions and subsequently theirmally curing the activated monomers according to he teachings of this invention. sally lower than those required for the direct thermal curing, with an advantage in the range from 50 to 110°C. This bird-stage curing also makes it possible to control the polymenzation in a particularly simple It is within the scope of this invention to include two-stage polymerization (curing), by first activating

genocides surfactants, pleascupers, and other additives as known to those stulled in the art can be added to the compositions of the invention. These can be added in an amount effective for their intended purpose agants, bodying agants, flatling agants, colorants, mert tillers, binders, blowing, agants, fungicides, bat-Adjunants such an schemes, pigments, abrasive granules, stabilizers, light stabilizers, anboxidants, flow Compositions of this invention, are useful for costings, loams, staped articles, adhesives, fitted or

lamborcad composites abrasives causiing and sealing compounds casting and molding compounds

RP 0 308 162 A3

EMERGY-MOUCED DUAL CURABLE LOW

PRILL OF THE STYBITTON

monomer and either polyuremane precursors or an epoxy mish. example, as protective coatings binders for magnetic media ancies comprising the composition of the invention are to an organometatic compound and an oxidizing agent and a re-This invention relates to an energy-polymerizable composi-

## lechground Of The Invention

solvents. There is an intense effort by law if activated in a controlled fashion tal contamination. These processes require a latent cald solids formulations to reduce or eliminate the use of such s Various polyment coatings and article

Patent Nos 4,521 545, and 4 582,8611 to as polyurethane procursors) using mermally ratent late baryamines is known in the art. Curing of polymerizabin Thermal curing or polyuremane precursors using

Polym Plast Technol Eng 1981 17 83-931, and price S.Y. TSAY, M. KOSHIDA, Y.S. Dung, S.L. COODER J. ACC. c successingly undown on Assurance (sedimenters) 4,549,945, and EP 28,696. Derment abstract). All of the salts, taritaryamine procursors, and siganobn compour modified resins, loss or slubon of wethere properties Photocuring of urothane (methacrylates is well kni-The dust curing of acrytate uremane precursor

precursors and acrylates (see U.S. Pat. 4.342 '93 : entrary photoactivated not are any methods ancient pages 46-55)

metallocene, such as lerrocene, can be used as a metal completies in the reaction between polyepunter 3,705,129) U/S Patent Nos 3,709,861 3,714,006 3 polymerization of eposide group-contained which the polymerization catalyst is a race teach the polymerization of epoxide groy The proviant discloses processes for the polythin

U.S. Patont No. 4.028.705 and the omum satts of Grand is described in U.S. Palent No. 3,794,578 and U.S. Pali polymenzation. Furthermore, the dicarbonyl chalates are in are disclosed in U.S. Pasent No. 4.058.4001, or a dicartas is disclosed in U.S. Patent No. 4 088 091. These onium saits and reducing agents U.S. Palent No. 4,216,298 teaches the thermal curity

omers have been described in U.S. Patent Nos. 4 15611 include onlyin salts combined with organic complexity Pladation dual curable compositions containing office

Energy, polymeritable compositions comprising in-cationically sensitive materies and the curry thereof in organometalisc compounds Nos 100.851, 1904 Dereent abstract, 094.915 1983 80 ST R.

SPONNIE Z

assed compounds, impregnishing and coating compounds, and other applications which

are known to those skilled in the eri

-excess pressing please and printed circuits from photopolymerizing compositions are well known in the art e ter example British Patent Specification No. 1,465,748). Compositions of this invention may be applied, preferably as a liquid, to a substrate such as sleet burtoon of articles weekd in the graphic arts such as printing plates and printed circuits. Methods of num, capper, cadmium, zinc. gless, paper, wood, or veriour plastic hims such as poly(ethylene and many be weathed with a solvent to remove the unpolymented portions while leaving the meniand, resoluble portions in place. Thus, compositions of this invention may be used in the using part of the costing, as by irradiation through a mask, those sections which have not been icked p. tyrvinyichloride), poly(grapytene), poly(ethylene), and the like," and irradiated

wife not be construed to unduly limit this invention. In the exemples, all parts are parts by weight unless Objects and advant als and amounts thereof receipt in these examples, as well as other conditions and rutals, e. As examples were prepared in ambient simosphere (presence of oxygon and water) ages of this invention are further illustrated by the following examples, but the

Case Grand 

appared using stantuard organismetatic synthetic techniques. The procedure used will be illustrated for the saure Charmical Company and used without further punification. The other compounds were wealthic compounds, [CpFe(COh]s. Mins(CO)10. Res(CO)10 and [CpMo(CO)11 were ob-

e.Sing of benanghanons in 200 mt. of freehly displied terrahydrohuran under an almosphere of argon. The by St. The reaction vessel was opered to air and the solvent removed under reduced pressure. The solid reduced to the amon as indicated by intrared spectroscopy (IR). To the solution of the anion was added. ser argen, 6.5 g of CiSnPhy as a solid. The reaction was stored until the anion was consumed as shown The asian. Coffe(CO)s, was produced by reducing 3.0g of [CoFe(CO)s]s with 0.41g of sodium and me to a similar assente all the cities materials in Table I were proposed. a was allowed to proceed for about 24 hours by which time the starting material had all been eas taken up in methylene chloride and passed down a short salica get column. Crytals wore and by ST, auction magnetic resonance spectroscopy (NAAR), elemental anim, is and meting g the mostrylene chloride under reduced pressure and adding help ...... The product

These compounds are used in subsequent example TABLE

COLORAGO	COMMENT COM	CoreCOLPANE,	Cofe(CO), Geria)	:	Compound	Cheac
SMS	****	67.68 51.0007	\$7.067.0 82.362.4	É	Elemental Analysis (ReportCalculated)	Characterization of Compounds
3434	1916	3332	3838	* 1	Analyses culated)	pounds
213-214	136136	1416	136-136		Point ( C)	

Several organismental components of the method of T.S. Poper, G. Willenson, Inorg. Nucl. Chem., 1956. 3, 104-124 () prepared according to the method of T.S. Poper, G. Willenson, Inorg. Nucl. Chem., 1956. 3, 104-124 () prepared according to the method of A. B. Manning, J. Organ (CO)<sub>3</sub>) was prepared according to the method of A. C. Vieta, E. Co. King, M. B. Bisnette, J. Organomet. Cham., 1984, 2, 15-37, to propere CpFetCOh: COPh). The provi of CoPtMey has been described in U.S. Palent No. 4,000,484 R. Comv. W. E. Douglas, J. Organomet. Chem., 1977, 135, 373, 386. The meth d of J. P. Priv. Wojcicki, J. Amer. Chem., Soc., 1985, 85, 4882 was used to prepare Coffe(CO)<sub>2</sub>(C) Phy), and that of Several organometatic compounds were prepared according to literature methods. CpWiCO1100H. These compounds are used in subsequent examples 1978, 157, 239 CoFe(CO); SiPh) was prepared according to the method of G. Cureau. E.

EXAMPLE 3 (Comparative)

of 0.01 g (CoFe(COh)), and 0.02 g Phyli PF; in 0.1 g gamma-buly/olactions was added 1.25 8.02 g.4.4 -methylanebs(cyclohexyhaccyanate) (Desmodur'ili W. a Mobay Corp. g polyethylane glycol MW400 (Carbowas Tu 400, Union Carbide, Danbury, CT) was prepared. To stock solution. The sample was photocured to a solid using a Kodak Nii Carousel Nii projector in 12 metal single bond in the curing agent to photocatelyze the formation of polytical Three samples were prepared as above, except the iron dimer and indomum salt were This example illustrates the use of an organometatic compound containing a by

0.03 g  $Ph_2l^{-}$   $PF_6^{-}$ . (a) was left in the dark while samples (b) and (c) were irradiated as above Ntollows: sample (a), 0.01.9 [CpFetCOhb., 0.03.9 Ph.). PF. - sample (b), 0.01.9 [CpFetCOi, L. s. three samples showed evidence of any curing, no obvious change in viscosity as evidence

### EXAMPLE 4 (Comparative)

0.01 g CpPt(CH1); (Cp = eta<sup>3</sup>-cyclopentadenyl) which had been dissolved in ca 0.15 mil pressure mercury arc lamp through Pyreaths. Complete cure was achieved within 12 mil  $\mathsf{CH}_{\mathsf{I}}\mathsf{Cl}_{\mathsf{I}}$  and gamma-bulyrolations. The resulting multius was stratheted with a Hanovis to 45 metrylene bis (cyclohexyl isocyanise)) and 0.72 g Carbonax 400 (polyot) were combined at single band in the curing agent to photocatalyze the formation of polyurethane. 0.52 g files: This example illustrates the use of an organometatic compound containing a transition

containing no curing agents. The resins are dual curing resins, and are claimed to form inter-The Herital Duo-CureTki reams are polypilalphaec polysocyanase and multihunctional activity This example describes the photocuring of Herisel Duo-Cure Na (Herisel Corp. Namesapons 1

networks (IPN's) when propt 'ly cured. cured in <30 minutes to a clear, hard mass. The other sample was coused on a longue de 0.5 parts (CpFe(CO)) b. and 1 part Phyli PFL - One sample was cured in the real using a 3 supposed to the suntain lamp. Curing occurred in 15 seconds, to yield a clear, hard, sanda intersed appears of this country's on sale please showed conversion of the socyanate to us Samples were prepared, 2.0 g in size, using 77 parts Hennel Duo-Cure 172A, 23 parts Duo

s are well known in the art inter \_ Hit Lats | Machoots of the trans on the same of the Care Survey Grane S 17. THE WAR SUC RESCHAPED : which have not been Lale Such AS Sleet والمعادرات والمراجع الماء

the shots which

at lifter Lungations and PRODUCT OF THE PROPERTY OF THE ATT AND LAND DI WORTH ILANDS CHAMPIONS DAS SHE

THE TOP COMPANY OF THE CHARLE STATE OF The upon correposate was and |CustorCOtal: -- Ob

- Send the Course Copies one A MARKET OF THE SPICE WAS RECORD. e are assert that in this product THE SERVICE PROPERTY OF SERVICE OF PROPERTY OF THE PARTY OF THE PA THE COMME present the end of the strength the amaginess of ergan The Las 0 410 of soom and

> prepared according to the method of T.S. Piper, G. Wilkinson, Ivorg. Nucl. Chem., 1956. 3, 104-124 (CuW-cCO)<sub>3</sub>) was prepared according to the method of R. Birdwhissell, P. Hackett, A.R. Manning, J. Organomet (CO)<sub>3</sub>) was prepared according to the method of G. Cuveau, E. Columet. R Corre W E Dougles, J Organomel Chem. 1977, 135, 373, 388 The method of J P Rober A Wopcodu. J Amer Chem. Soc. 1988, 88, 4852 was used to prepare CpFe(C0)<sub>2</sub>(C)-Ph<sub>2</sub>), and that of R Rungles, M. B. Barrette, J Organomel Chem. 1994, 2, 15-37, to prepare CpFe(C0)<sub>2</sub> COPh). The preparal his of Cortilles has been described in U.S. Patent No. 7,800,484 Several organometatic compounds were prepared according to literature methods. CpW(CO)<sub>1</sub>(CH<sub>1</sub>) was

EXAMPLE 3 (Comparative)

These compounds are used in subsequent examples

8 02 g 4.4 -metrylenebis(cyciohanytisucyanase) (Desmodur Tu W. a Mobay Corp., Pittsburgh, PA) and 11-20 of 0.01 g [CpFe(COb.)), and 0.02 g Phyli PF; In 0.1 g gamma-bullyrolactions was added 1.25 g of the g polyethylene glycol tereson (Carbonas Tu 400, Union Carbide, Danbury, CT) was prepared. To a solution metal single bond in the curing agent to photocatalyze the formation of polyurethane. A stock solution of 0.03 g Phyli PF<sub>6.7.</sub> (a) was left in the dark while samples (b) and (c) were irradiated as above. None of the tollows sample (a), 0.01 g (CpFe(CO)z), 0.03 g Phyl<sup>\*</sup> PF<sub>\*</sub><sup>-</sup>, sample (b), 0.01 g (CpFe(CO)z), sample (c). stock solution. The sample was photocured to a solid using a Kodak Till CarouselTill projector in 12 minutes. This example illustrates the use of an organometatic compound containing a transition metal-transition Three samples were prepared as above, except the non-dimer and lodonium salt were added as

EXAMPLE 4 (Comparative)

thee samples showed endence of any curing, no obvious change in viscosity as evidence, after 20

single bond in the curing agent to photocatalyze the formation of polyurethane. 0.52 g Desmodur W (4.4. 0.01 g CoPNCH1); (Cp = ets)-cyclopentackenyl) which had been dissolved in ca. 0.15 ml of a misture of pessure mercury arc temp through PyrasiTu. Complete cure was achieved within 12 minutes irradiation ON-Or, and gamma-busyrolactors. The resulting musture was krackated with a HanoviaTil 450 watt medium methylana bis (cyclohexyl isocyanate)) and 0.72 g Carbowax 400 (polyd) were combined and added to ca This example shustrees the use of an organometalic compound containing a transition metal-carbon

#### EXAMPLES

The Haster Duo-Cuse'to reams are polyolalipheac polyeocyands and multifunctional acryllala systems The example describes the photocuring of Henhall Duo-Cure Tu (Henhall Corp., Minneapolis, MRI) resint turning no curring agains. The reports are dual curring reports, and are claimed to form interporterating

F\_MI. . .

. Se 100

ķ

10-1 H

0.5 parts (CoFetCOta)s, and 1 part Phyli PFLT. One sample was curied in the vial using a suntan lamp. cused as <3.0 minutes to a class. Need mass. The other sample was coated on a tongue depressor and extend special of the coatings on sell place phowed conversion of the vocyands to wellhare upon imposed to the sumble lamp Curving occurred in 15 seconds, to yield a clear, hard, sandable costing Sumpes were prepared: 20 g in 1231, using 77 parts Hankel Duo-Cure 172A, 23 parts Duo-Cure 172B.

exposure to suscept cadeston

"polydi" medite an aliphatic or aromatic compound containing "polyleocyanida" moans an alipheac or aromalic (socyanida n 'onum satt' means sats of casonic compounds such so die

becaled Disclosure of the Invention

De weight parcent of eather polyurethese precursors or an eq posson comprising in the range of \$8 to 1 weight percent afore specifically, in a preferred embodiment this river

therefor, the curing agent comprising in structure in an organometatic compound having the structure

ר.ר.ר.

substantiated and unsubst L' represents nonc, or 1 to 12 ligende contributing prom contributing 2 to 12 protections to the village of M. Lan be the 1. agne-stactions strected from moro-. Or, and bi-dentals meeted from subsenied and unsubsenied acyclic and ed carbocyci

L3 represents north, or 1 to 12 significal that can be the MELVE, VIE, VIEE, and VIEE (COMMONNY returned to as to ose agree electron each to the valence shad of each M ) the valence short of M HE I ID & Of the same or different metal at-

with the provide that said organization [2] and with the provide that L', L2, L3 and M are chose 2) an oraum suit conducing agent housing the store

379A576 3800.008 4028.705 4008.401 4080 A is an organic casion selected from those destrict from Oppenyhodomum, beginery/buildinum and pilopreferably selected from descrives, lodon

CUSO, MET PAT BAT BATON AND S X is an awar. The countered of the one train Groups MA to VA of the Period hatogenities michel or mentations, such as CH1801 due of 1 to 6. Protectily, the mater hose in which X has the formula OZy count or michal and the metabolic protocols are propultings and recess comes and the the and your Preferency, the National Z, is chissen of II.

This curing against can be present in the range of total composition. The ratio of organismetalist comfuweight, preserably 5 1 to 1 8 by weight This present museon also provides a process griers in combination such one of polyviethers i

precuisors or an appear compound. estate ero sees to bettern a Bubroad (s)

and absence of O<sub>2</sub> using translatin metal-translation metal bond contuning organometalic compounds and This eliample illustrates the photocuring of polyurethene precursors to polyurethenes in the presence

and a water inhaned litter. Both samples cured after 10.0 minutes irradiation. This demonstrates that in the were irradiated simultaneously with the output of a 450 watt Hanovia mercury lamp, hitered through Pyrex W (4.4 - mathylanabialcyclohanyllaocyanate)), and 1 17 g polyethylaneglycol (MW = 400) was divided in had. One had was bubbled such No for 2-3 minutes, the other last open to the atmosphere. Both samples presence of onum salt, curing occurs with or without  $O_2$  present. onum seit as curing age A mixture of 10 mg (CoFe(COh.b. 30 mg Phyl." PFc.", 0.1 g gamma-butyrolactions, 0.83 g Desmodurts.

### EXAMPLE 7 (Comparative)

3 using 1.25 g of the stock tolution, 0.01 g neutral metal-metal bonded compound and 0.015 g Ph<sub>2</sub>li PFs Desmodur W. 1.9 parts butanedial, and 0.5 parts trimediyloloropane. Samples were prepared as in Example in 0.05 g gamma-butyrotactorie, tradiations were carried out on a 450 W Hanovia medium pressure organometalic compounds and lodonium and sulforium satts. A stock solution was prepared from 7 parts morcury are through Pyrisi. Alternatively, these compositions can be cured therm\*';-This exemple describes the photocuming of polyurethene procursors using transition metal containing

TABLE II

			_
[CofCO]» b [CoFe(CO]» b [Mer(CO]» b [Co.(CO]» 2 [CoMO(CO]» b Fe <sub>21</sub> (CO)»		Organometatic Compound	lodonium and Sulfornum Salts
8.0 90 12-20 20-40 40-55 55-87 Ca. 90	Ph <sub>2</sub> 1	Cure time, minutes	utonum
>100 20-25 7-12 20-46 95-88	Phys.	minutes	Sans

### EVALUPLE 8 (Comparative)

Carbonian 400 and shating well before use. Samples were prepared by dissolving 10 mg catalyst and 20 contain transfers metal-carbon bonds which are effective in the curing agent for polyurethane precursors. A stock solution of polyurethers precursors was prepared by mixing 23.1 g Desmodur W and 32.5 g under the lamp sectiod ca. 50°C within 10 min. The time to a vecocity increase is noted in Table III, and dads, and samples used then eradiated under a Henova Quartz Usiky Lamp. The temporature of samples ang digham/hodonium haushuorophosphate (if used) in  $0.2\,g$  CH<sub>2</sub>G<sub>2</sub>,  $2.0\,g$  stock solution was added in the "cure time" is the time for a sample to become so viscous that it would not flow. "Partial cure" is indicated when, we'vn 10 min madeston, the sample became more viscous but would still flow This provides further examples of bicomponent curing agents wherein organometalic compounds

#### EP 0 304 162 A2

#### TABLE II

a included for purposes of comparison	CoPthés CoPthés + rodomum CoW(CO)sée + rodomum CoW(CO)sée + rodomum ((Péé,Ph);Phés(acetones)* PFi * (CoFe(CO)s); + rodomum*			Curing of Polyuretherie Precursors
	9 3 3 8 7	Viscosity Incresse	Cure Rates, me	Durators .
	2 2 2 2 2 2 2	Cired	3	

control the organometallic oxidizing agent ratio. provide a suitable quickzing agent. However, the use of onlum salts is preferred since it is much ear The data show curing occurs with or without iodoinum safts, in some cases, adventibous oxyge:

## EXAMPLE 9 (Comparative)

30 polymer was tested by placing a few drops of the sample in about 2 mL methanol Formation of added in the dark, and samples were then irradiated under a Hanovia Quartz Utility tamp, limbal liand 20 mg diphenyliodonium heisthuorophosphate (f. used) in 0.2 g CH<sub>2</sub>Cl<sub>2</sub> 2.0 g cycloheisene in a transition metal-carbon bond to cure eposies. Each sample was prepared by dissolving 10 mg indicated that polymer had formed. Further polymerization resulted in a viscocity increase in " This example describes the use of the curing agent containing an organometatic compound or

Results are indicated in Table IV

#### TABLE N

a included for proposes of comparison.	CoPtides Coptides + odonium CoW(CO)side + iodonium (Pales Philip Philes (acatomis)) + PFs.* (Copfie(CO)sis + iodonium*	Curing Agent
3	70 Cure	Precipitate formed, man
	S CAR	Viscosity uncreased, min.

### EXAMPLE 10 (Comparative)

organe metallic compound and/or 0.20g diphenyllodonium hexaliush type organometalist compounds and onium east to photometate the cure of apostes are provided from acoton-viscoproperiot. Then, the following operations were carried out under subdivise by tests were carried out in the following matrices: Into a glass was weighed out U-10g of the gamma-butyrolectore. 2.0g cycloheueine aurde (Aldrich Chem eponycyclohenylmethyl-3,4-eponycyclohemene ceithonylete (EML-4281, Utron Ceithde Compeny Examples of the ability of curing against containing transition metal-transition metal-to-rived HELE COMPANY, CHEMICAL SOS

the standards of the re-... anes in the presence

THE OF THE SECURITY OF THE PARTY OF THE . atmosphere Both samples attices 0.83 g Desmodurity 1.17 = 400) was divided in and titlered through Pyres

In and and 0.015 9 Phyli Pf. s were prepared as in Example co was prepared from 7 parts transition metal containing W Hanova medium pressure

control the organismetallic exidizing agent rate.

A. 4.

TABLE #

Curing of Polyurethane Precursors  Cure Rates. min Viscosity Cured Incresse	Series Se	7 7 30 30 13	Copetities  Copetities + rodonium  Copetities + rodonium  Copetities + rodonium  ((pties/Ph); Pties (accisions)) + PFs - re  (Copeticoly)]; + rodonium
7 2	3	Increase	
Curing of Polyurethere Precursors  Cure Rass. min	Cured	Viscosity	
Curing of Polyurethane Precursors	8. mm ;	Cure Rate	
		cursors	Curing of Polyurethane Pre

provide a suitable oxidizing agent. However, the use of onlum salts is preferred since it is much easier to The data show curing occurs with or without iodonium salts. In some cases, adventibous oxygen can

a included for purposes of comparison

### EXAMPLE 9 (Comparative)

indicated that polymer had formed. Further polymerization resulted in a viscocity increase in the sample polymer was tested by placing a few drops of the sample in about 2 mL methanol. Formation of precipitate and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH<sub>2</sub>Cl<sub>2</sub>, 2.0 g cyclohexene oxide was a transition metal-carbon bond to cure eposies. Each sample was prepared by dissolving 10 mg catalyst added in the dark, and samples were then irradiated under a Hanovia Quartz Utility lamp, Initial formation of Results are indicated in Table IV This example describes the use of the curing agent containing an organometalist compound containing

TABLE N

Precipitate Viscosity formed min increased min no cure no cure 3.5 3.0 2 no further cure 30 30
--

a included for proposes of comparison.

### EXAMPLE 10 (Comparative)

LIGHT for polyurethans precursors A visitein organometalisc compounds

3: 3 Desmodur W and \$26.9

3 Stock solution was added in the tips living 10 mg catalyst and 20

amp. The temperature of samples

rease is rolled in Table M. and

"N. "Partial cure" is indicated

· 41 / 100#

organs nessins compound and/or 0.20g diphenytodonium heusiluorophosphate (3M Company, recrystalised type organometatic compounds and onlum salt to photomissis the cure of epoxies are provided here. The from acotone-isoproperch. Then, the following operations were carried out under subdued light, 0.3g of ness were carned out in the following manner: Into a glass visit were weighed out 0.10g of the desired Examples of the stainty of curing agent containing transition metal-transition metal bonded and M-L<sup>3</sup> u-butyrotectore, 2.0g cycloherene oxide (Autrich Chemical Company, distribut). 5.0g of 3. 4-cyclohers/ene/1.4-eponycycloherene carbonylese (ERL-4221, Union Carbide Company) were of-

> (CO), MinPoPh) Cofe(CO)2PoPh) COICON Mo-MAYCON Cp(COhW-MolCOhCo CpW(CO);Ma (CO), ReSnPhi Cp(CO);Mo-Re(CO); (CO), Man J. Smann (CO), Mn-Fe(CO) Co Cp(CO):Mo-Fe(CO):Co COICONW-CoICON Cp(CO):Mo-Co(CO) COICON W-Re(CO) CO(CO); W-May(CO);

COICONW-FOICON CO CpMo(COnPPh) b Ang(CO) (PPIn) is In<sub>2</sub>(CO)<sub>3</sub>PPh<sub>3</sub>

COM Man-ResCOM Fe<sub>3</sub>(CO): 2 a<sub>d2</sub>(CO)<sub>b</sub>(1.10-phenanthroline) Ang(CO) (1.10-phonen te<sub>2</sub>(CO)<sub>8</sub>(2.2 -biquinoline) Cofe(CO); kSi

P13(CO): 2

093(CO):2

Fe2Ru(CO): 2 Rus(CO)10(PhzP-CHzCHz-PPhz) Pu<sub>2</sub>(CO), PPP13 CoFe(CO); CH; Ph Contico)b 8

Cofe(CO);(SiPh) CoFe(CO)z(COPh) COICON Fo-FolCOXPPh J/Co MaCo)Polas CP Fe(CO) b

Cp(COhMo-Mo(COh(PPh.)Cp (May SiCo)Pthias 

The phany Cp. is east-pentamentylcyclopentacientyl Co is east cycloportaclemy

Suitable compounds containing at least one ethylenically-un A wide venery of monomers can be energy polymerite

andror oligomens such as (mech)acrylates. (mech)acrylamidos crylate, parkatrybratel tracrylate, parkatrybratel telesaccyki indurgoing addition polymerization. Such monomers inco reductylese of polyethylese glycols of malecular warps 20 ylanaghycol diacrylcia. Inadhylanaghycol dimediacrylais man, staenyi acnylama, aliyi acnylama. Olyomrol diautrylami. U acrylates such as mothyl acrylate, methyl methacrylate i hecryleta, transfrytotorogene tracryleta, 1.2.4-bulgretii mere such as those of U.S. Patent No. 4.883.374. and bud 1-(2-acrytony))-0-admonygatemytic e tra-hydroxyddryhaacydrus

Photombatiod Cure Times of Epony and Acrylate Compusitions

Amoda

(Cose(CO)) b odonum

Š

ğ

Pe/(CO): Mnz(CO)·s Mm<sub>2</sub>(CO)- s Coffe(CO), l Catalysi System

ğ ğ

8 . 8 8 . 8

Rez (CO): 3 (CO)(CO)

Co,(CO) 1000mi

**COONWIT** 

Co.(CO) codonium Co.(CC)

ģ

PLOT TON Q a Cure bine in securids

or picts up no cotton threads. This test establishes the time required to cure the coating. Under the critands subbed polyester (3M Company) using a 822 title wound rod. The sample costings were exposed. conditions of this test the aphenylodomum hazaffuorophosphate alone requires greater than 10 min to in air, to a 275 wast G.E. sunlamp at a distance of 10cm. The time to "set to cotton" is recorded in Table V. ded to prepare the coating solution. The solutions were coased onto 78 micrometers (3 mil) polyvinylidens that is the time needed to cure the coating so that when it is touched with incotton ball it leaves no smear

TABLE V

	_	7
	Domina	Photoinitiation
No Onum Salt Added	Cure 1	Photoinitiation of Eposity Cure
Onium Salt Added	me.	
	No Onum Salt Added	

č

## EXAMPLE 11 (Comparative)

grother epoxy and or acrylate composition. The organometallic compound, with and without the critical salt actyliae eas distribed from hydoquinone and stored cold until leady for use. Cyclone ene outline was used as occamed. Irom. Addich. The organometalic compounds were obtained from commercial sources Denenylocomum resistuorophosphase was recrystalized from acetone isopropanol. All experiments were was provolyzed in presence of an epoxy or acrylate. The specific system used is as follows methyl-To turber permonstrate the activity of the curing agent a series of experiments were carried out in

gone as 100% solids except as noted sair along aim 2 g of the desiren monomer. For the actifulte tests, the solutions were purged with N. for 60 sures represent the time required to reach the same degree of cure usually geration of the solution sec before and community during the photolysis. The epoxy tests were performed without purpling lives Assenatively the acrylista compositions can be cured thermally in a small lead eas paced 0.02 g of the organometalic compound with without 0.14 g of the issorrium The light source was one 15 wast daylight shorescent bulb in Table VI below the cure

3 10% by attigamma-bulyrisactions added c Reacted in the dark upon inverty

## EXAMPLE 12 IL. INLAUDINE

r.	•	
	This invariable demonstrates the admity of translated information interests and demonstrated demonstrated to photonitate the cure of officeres any making the cure of officeres and officeres into a positive desired organization of odd in the officeres incomment of odd of the desired organization of odd officeres incompanies. Their the information are the company of odd of the observed organization of odd on the odd officeres incompanies. The odd officeres of odd officeres odd odd officeres odd officeres odd officeres odd odd officeres odd odd officeres odd odd odd odd odd odd odd odd odd od	
A ARA	Carried II (carried Communication)	
ياملون ويون دواسلوه ودان	The color of the c	•
yealer than	Trymann of the control of the contro	
19 1941 1	an office of the control of the cont	

TABLE VI

Acrylate >600 > 600
---------------------

a Cure bine in seconds

b Not done c Reacted in the dark upon mixing

d 10° by at gamma-bulyrolactore added

### EXAMPLE 12 (Cumporative)

This example demonstrates the charty of transition metal-transition model bonded or MLT typo or parameters compounds to protontable the cure of ethirencelly unstaturated compounds in the protonce parameters. The tests were corried out in the toloring months to to gives will occupate that the protonce of the desired approximate the cure of 10g optimish populations are corried out which of the desired approximate them experienced to the test toloring operations are corried out which company is according to the test toloring special test according to the test toloring to the test toloring special test according to the test of the test of

CoFe(CO); SnPh; CoFe(CO); SnPh; CoFe(CO); GoPh; (CoFe(CO); I: SnPh; Mn; (CO); (CO), MnSnPh; ((CO), MnSnPh; ((CO), MnSnPh; ((CO), MnSnPh; (CoMo(CO); SnPh;		Organometallic	Curing of Ethylenically Unsaturated Monomers
>600 >600 >600 >600 >600 300 60 500 >600 >600	No Onium San Added	Cure 1	y Unsaturated N
24.00 8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9	Onum Salt Added	T <sub>i</sub> me <sup>6</sup>	Aonomers

a time in seconds to cure b saturated solution <0.01g dissolved

## EXAMPLE 13 (Comparative)

Further examples of the curing of ethylenically unsaturated monomer (25.9 of nentweryteinto) terracrytate in 225g acetonitrie) or epoxy monomer (cyclohexene binde) are provided it all curable tetracrytate in 225g acetonitrie) or epoxy monomer (cyclohexene binde) are provided it all curable composition consisted of 0.01g of the organometallic compound or 0.02g of dipher, adonumin test composition consisted of 0.01g of the organometallic compound added to ether monomer. The light sources allow oppositive or these same amounts of both compounds added to ether monomer. The light sources used on the exposition of the polymer known as desected by carousel Projector or the projector with a 440 nm filter. The initiation of polymerization was desected by carousel Projector or the projector with a 440 nm filter. The initiation of the polymer from a 2% course of projector or the acrylate and for the epoxy, the procretation of the polymer from a 2% primornal methanol solution. Free radical systems were purged with N<sub>1</sub> for 2 minutes before and continues of the six mithout purging. Samples are systems were purged with N<sub>2</sub> for 2 minutes before and continues of the polymer free cationic samples were left open to the air mithout purging. Samples are systems were left open to the air mithout purging.

TABLE VIII

Photominated Cure Times of Epoxy and Acrylate Compositions

WCAA Compositor		
Curing Agent	VEO 9	ACTAIN
		•
Coreconi	8	\$
[CpFe(CO); ]; rodomum	ğ 8	
		•
Man (CO)	100	-
Min <sub>2</sub> (CO)- a rodomum:	, 180°	
The bridge Green in Ser. H		

• Blacture used as the light source stress

d add rim hiter used seth the projector

b Unahered projector as 12 control or communicate stored no communicate stored no conditions.

EXAMPLE 14 (Comparative)

Examples of the photocuring of emyterically unsalurated mineral bond containing organization compounds and odonium is made bond containing organization (a methyl acrylate containing amples when proposed as 1.0 g methyl acrylate containing complex and 0.015 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and odonium is proposed and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and odonium is proposed and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and odonium is proposed as 1.0 g methyl acrylate containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g Phyl PF. Up to 0.05 g but rotationer containing and 0.05 g but rotationer co

TABLE IX

	Curra u	Curing of Ethylanically-Undehicator, N.	Indeburator: N
8-8-E	" <b>Z</b> l	Condeons	
3	- 1		
ē	DegCOh la	Ė	Mark No.
8	May (CO):		
5	(CoMorCOn la	Ē	
-	Pa(CO)	i	
	Coalcon	}	Care Guita
C	Concor	1	

EXAMPLE 18 (Cumparabre)

This example describes the curry of employmently unadards burded organization. Computate Each sample was prepared

TABLE VIII

Fe(CO): 2: rodonium 9180 92 92 92 92 92 92 92 92 92 92 92 92 92
---

a Cure times given in seconds:

b Unintered projector as light source c. The diphenyliodonium salt showed no indication of polymenization by

tiself under these same conditions d 440 nm titler used with the projector

e Blacklite used as the light source, about 360 nm.

## EXAMPLE 14 (Comparative)

Examples of the photocuring of emylenically unsaturated monomers using transition metal-transition

Alternatively, compositions could be cured thermally metal bond containing organometalic compounds and iodonium salts are given here.

Samples, were prepared as 1.0.9 methyl acrylate containing 0.01.9 metal-metal bond, containing 0.01.9 metal-me the photocatalyst systems. Samples here bubbled with N2 and irradiated using a Kodak Carousel skide projector, with a 360 nm cutoff litter, and the time required to cure the sample recorded in Table IX.

and the either monomer. The light sources at in it pulymorization was detected by

. ... truths and for the visible, a Kodak

THE NUMBER OF THE PROPERTY OF

... I die snown in Table VIII

transin of the polymer from a 2\*-. ... air without purging. Sample size

1.000 of doher oddraum her

are provided ...

remaining (25.9 of neminary divinol

#### TABLE IX

ICOFe(CO):b Man;(CO):a ICOMO(CO):b IRM(CO):2 CO2(CO):	Compound and PFs -	£
Dark State of the	Conditions	
30 sec, slow dark reaction 30 sec, no dark reaction 45 sec, no dark reaction 8 min, no dark reaction Minutes, slow dark reaction Cures during decryganation	Cuie Time	R. B.

bonded organometatic compounds. Each sample was prepared by deschang 10 mg catalyst and 20 mg This example describes the curing of ethylenically uneabseated managers with transition materials and second of the curing of ethylenically uneabseated managers with transition materials and the curing of ethylenically uneabseated managers with transition materials.

Cure Times: Ph toinitiated Curing & Polyurethane P

TABLE XI

Epoxies and Vinyl Monomers ith Transition Net Group IVA Compounds

digitally obtained there is no compositions of the property of

TABLE X

	CoPrises + ode Cow(CO)s Me Cow(CO)s Me Cow(CO)s b	Curing of Et
for numbers of comparison	• iodonum • iodonum aMe iodonum	Curing of Ethylenically Unsaturated Monomer Curing Agent Cure time, mi
d comparison		Saturated Mor
3	15 (Hanovia) 6 (Kodak) no cure 3.5 0.5 (dark cure)	Cure time, min

## EXAMPLE 16 (Comparative)

This auampte describes the use of [CpW(CO)<sub>1</sub>b to cure polyurethane precursors, epoxies of ethylenically unsaturated monomers. Each sample contained 0.01 g -{CpW(CO)<sub>1</sub>b and 0.02 g ethylenically unsaturated monomers (if used) in 0.25 g pamma-butyrolactions, to which was added 2.0 g ephylenylectorium haushurorphosphase (if used) in 0.25 g pamma-butyrolactions, to which was added 2.0 g precursor or monomer in a vial, irradiation was then performed with a Kodak Carousel Projector (in inches), or monomer in a vial, irradiation was then precursor stock solution (prepared as in Example 4). In precursor or absence of online salt, partial curing to produce a clear solution; occurred in the presence or absence of online salt, partial curing to produce a clear solution; occurred in the presence or absence of online salt, partial curing to produce a clear solution; occurred in the presence or absence of online salt, partial curing to produce a clear solution; occurred in the presence or absence of online salt, partial curing to produce a clear solution; occurred in the presence of absence of online salt, partial curing to produce a clear solution; occurred in a salt partial curing to produce a clear solution; occurred in a salt partial curing to produce a clear solution; occurred in a salt partial curing to produce a clear solution; occurred in a salt partial curing to produce a clear solution; occurred in 2 hours.

Cpre(CO)2(PbPh3)/iodonium

33 min (W)h

30 Cul.

Cp# (CO) 2 (PbPh 3)

when cycloheseneousde was used, and the curing agent consisted of [CpW(CO)s]s and online salt, when cycloheseneousde was used within 7 min of irradiation, upprous, exchemic curing occurred within 7 min of irradiation to curing occurred in the absence of online salt. With these measures was used as monomer, no curing occurred in the absence of online salt present, the sample became viscous within 4 min and solid within 8 min of irradiation time patients as the present, the sample became viscous within 4 min and solid within 8 min of irradiation time.

## EXAMPLE 17 (Comparative)

To demonstrate the using of the curing agent for curing of polyurethane precursors, episities and unity monomers for the case where the organometalist compound contains a single bond between a transition encorrect for the case where the organometalist compound contains a single bond polyurethane. It is belowing samples were prepared in a vial, 0.01 g of organometalist compound, and 0.75 g of parametrizations. The organometalist compound was complete compound. O.02 g of dephiesiphodometric solution was added in reduced light, the vial was capped, and the 2.9 g of polyurethane percursors or monomer was added in reduced light, the vial was a distance of nine 2.9 g of polyurethane because of a Kodait Carousel projector hand with a 350 nm catalit have at a distance of nine 2.9 g of polyurethane because (about 25°C). Persourer distants and any supermental variations and and catality and at room temperature (about 25°C).

Cpre(CO)2(CH2Ph)/iodonium Cpre(CO)2(CH2Ph) Catalyst System Cpre(CO)2(SiPh3)/iodonium Cpre(CO)2(SiPh3) Cpre(CO)2(COPh) [Cpro(CO)2)2 Cpre(CO)2(COPh)/iodonium [Cpre(CO)2]2/lodoniumd cpre(co)2(GePh3) cpre(co)2(SaPh) Cpre(CO)2(GEPh3)/iodonius cpre(CO)2(SnPh3)/iodonium PolyUrethane 130 min (W)\* 120 min (V) 120 min (V) 40 min (Y) 40 min (V) 60 min (W) 45 min (V)" 45 min (V)" 36 min (V)" 36 min (V)" 36 min (V)h 36 min (S)h 45 min (S)h 30 ... 13 =10 2 -10 5 210 2.75 mi

hus then madated for 15 mm under the required for a sample to solidit . ...... Carousel Projector containing a . Lutitled through the sample for 2 Lactione 20 g memyl accylate

(Baristan) יוי ונחים שוט Minority TOTAL CLASS

produce a clear sobleon, occurred in 2 hour issur stock schiedn (prepared as in Example 4). arma-budyrolactors to which was added 2.0 g numbed 0.01 g [ConstCOh]; and 0.02 9 HILLIGASS IN VISCOSILY OCCUPIED irrad with a Kodak Carousel Projector (9 inches tire polyuremans precursors epowes or

by occurred in the absence of onum salt. With ions consisted of [Control); b and onum salt and soud within 8 min of irradiation time.

tien with a 360 nm cutoff taler at a distance of name so in reduced light the visit was capped and the Fair of used as indicated below) and 0.25.9 of reverse processing in a way 0.01.9 of organization contains a single bond between a transform at of the organometatic compound was compl ing or polyuromane practitions repoined and very at Julians and any experiments variations are

TABLE XI

[Cpr.(CO)212 Cpre(CO)2(CH2Ph)/iodoniu Catalyst System Cpre (CO) 2 (CH2Ph) Cpre(CO)2(COPh)/iodonium CpFe(CO)2(COPh) Cpra(CO)2(SnPh3) Cpre(CO)2(GEPh3)/iodonium Cpre(CO)2(GePh3) Cppe(CO)2(SiPh3)/iodonium Cpre(co)2(SiPh3) [CpFe(CO)2]2/iodoniumd Cure Times: Photoinitiated Curing of Polyurethane Precursors Cpre(CO)2(SnPh3)/iodonium Cpre(CO)2(PbPh3)/iodonium Cpre(CO)2(PbPh3) Epoxies and Vinyl Monomers with Transition Metal-Group IVA Compounds PolyUrethane 120 min (VV) 120 min (V) 120 min (V) 40 min (V) 40 min (V) 60 min (VV) 45 min (V)h 45 min (V)h 36 min (V)h 33 min (VV)h 36 min (V)h 45 min (S)h 36 min (V)h 36 min (S)h Epoxy 30 500 12 min • no cure . no cure 5 21 5 110 2 min • 2.75 min no cure • -48 hr 9 23 min no cure 48 hr 9 no cure DO CALS no cure 1.8 min no cure no cure no cure TO CUTO

Polyurethane precursors are from a stock solution consisting of 23.1 g of Desmodur TM W and 32.6 g of Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V = viscous, in parentheses of extent of cure, where V = viscous,

Wo wery viscous, S = solid.

Monomer is cyclohexene oxide, purified by distillation.

Monomer is defined as the time necessary to observe formation of precipitate when one drop of sample is placed in 2 ml of methanol.

Monomer is methyl acrylate, purified prior to use by distillation under reduced pressure. After monomer addition but before irradiation, samples were addition but before irradiation, samples were deoxygenated by bubbling a stream of nitrogen gas through the solution for 2 min, with care being taken to prevent any light from reaching the sample during deoxygenation. Cure is defined by an increase in solution viscosity or a sudden exotherm indicating solution viscosity or a sudden exotherm indicating rapid polymerization (also accompanied by a sudden

increase in viscosity).

d. Included for purposes of comparison to data in other

e. 60 min irradiation with Carousel Projector, followed by 60 minutes of irradiation in room (fluorescent) light.

g. This particular combination was not tested.
g. 30 minutes irradiation with Kodak projector, following
by 30 minutes irradiation under a Hanovia Quartz
Utility Lamp (6 inches from bulb), followed by sample
storage/irradiation in room (fluorescent) light.
h. Irradiation with Hanovia Quartz Utility Lamp (15 cm
h. from bulb) in place of the Kodak Projector.

EXAMPLE 18

The example distribus the dual curry of polyurations procurers and environcelly-unexament

emonomers using the cursing agent (CpFe(CU)s) PTUs! PTV:

Sumples 1.26 g in sub. were proposed from etock tolkators of 2.00 parts Deprenduct's W. (4.1).

Sumples 1.26 g in sub. were proposed from etock tolkators of 2.00 parts Deprenduct's action and tolkators of 2.02 parts polyathylemotylood (0.04 = 400), 6.0 parts methyl actricis;

supply deptices, and 8.00 parts (CpFe(CO)s). To half of this stock tolkator was added 0.002 parts Ptyl.

pF<sub>6</sub> Mole ratios for iodomium satt iron dimer \* 2.1 NCO OH \* 1.0° cm iodomium satt \* 1.2°s. Samples were irradiated smultaneously using 380 pm 10 min, then analyzed by 400 MHz. 'Hinuclear magnetic resonance spectrost are listed in Table XII. Curing agents compraing other combinations of risponium satts can be used in place of [OpfielCOh] and PhyliPF<sub>6</sub>, respectively.

#### TABLE XI

		<i>.</i>
1111	S	D.
Dark Irradusion decrygenated Dark Irradusion, decrygenated Irradusion, decrygenated	Condeone	Dual Curing of Polyureinane Precursors and Ethylenical Unsaturated Monomers
ž 3 🕽	Conversion to po	ors and Ethy
•	10 p	BOX.

#### EXAMPLE 10

and was prepared. To a 10g sample of the minture was added  $0^{\,\prime\prime}$ Gelation times will not show that both monor tradition time was 2 metudat. The experiment was carried out in the following matrier: A 1:1 with mini t mun before and contin nuclear magnetic resor. that of polymer plus mon plien. The amount of polyme specified amounts of both con This evampte demonstrates simus spraphagham (0.024g with the non dir er 0 - spectroscopy to differentiate the two polymuptly during irradiation. The light source +4 The results of the study are shown in Tuounds, in a small wall was placed 2 mil Party and compl secus curing of adhyterically uns. name have reacted at the ad by the rate of

#### TALL XI

May (CO) - Indianam May (CO) - ICO (CO) - Indianam (Co) - Indianam	Curing Against	Percent Converses to P
£9.88	Epomy	1
+ ĝ 6 8 5	Acrylato	S NEWS

b Hadil's taken on a 489 Miles metrument b Harra desected in the Malfil

As can to seen from the MERR results. The tydelen officially in polymeration sumultaneously. County against comprising their combine and county to the county and county to the county t

EP 0 308 182 A2

TM W and 32.6 g of followed by an indication cure, where V = visc us.

hen one drop f sample is

pressure. After monomer action, sampl s were a stream f nitrogen gas a stream f nitrogen gas a min, with care being taken reaching the sample during efined by an incr ase in udden exotherm indicating o accompanied by a sudden

comparison to data in other

in room (fluorescent) lightion was not tested.
ion under a Hanovia Quartz
rom bulb), followed by sample
rom bulb), followed by sample
oum (fluoresc nt) light.
Ouartz Utility Lamp (15 cm
he Kodak Pro) ctor.

THE PROPERTY AND OTHER PROPERTY OF THE PROPERT

spinitions of 208 parts Deamodurity W (4.4) in parts of the parts of t

PF<sub>6</sub><sup>-</sup> Nobe ratios for indonum salt iron dimer = 2.1, NCO-OH = 1.0, weight % iron dimer = 0.5%, indonum salt = 1.2%. Samples were irradiated simultaneously using 368 nm BlakRay builts (15 watts) for 10 mm, then analyzed by 400 MHz. 'H nuclear magnetic resonance spectroscopy Conversions to polymer are lasted in Table XII. Curing agents comprising other combinations of organometalitic compounds and only salts can be used in place of (CpFe(CO)<sub>2</sub>)<sub>2</sub> and (Pt<sub>2</sub>IPF<sub>6</sub>, respectively).

#### TABLE XII

Phyl Dark Phyl Irradiation decayge Phyl Irradiation decayge None Irradiation None Irradiation decayge	Onium C Satt	Dual Curing of Polyuretha Unsature
deaxygenated deaxygenated	Conditions.	styurethane Precursors Umsaturated Monomers
783 I	Conversion to poly: Acrylate Uretra	ors and Eth
56% 9% 11% 75%	n to polym	and Ethylenically

#### EXAMPLE 19

This example demonstrates simultaneous curing of ethylenically unsaturated monomers and eposition. Gelation times with not show that both monomors have reacted at the same time. It is possible to use nuclear magnetic resor. In spectroscopy to differentiate the two polymers in the presence of each other. The experiment was carried out in the following manner: A 1/1, w/w; musture of methyl acrylatercycloheamers obtained and the prepared. To a 10g sample of this minture was added 0.01g of [Coffe(COta) or May(COta) ophisinylodorium hasafulorophosphase (0.024g with the iron direct 0.03 g with the manganese dimen) or specified amounts of both compounds. In a small visit was placed 2 min of the sample and it was purged for specified amounts of both compounds. In a small visit was placed 2 min of the sample and it was purged to the before and continuely, during installation. The light source was five 15 wast (8.5 backing balas, trackation time was 2 minutes; furning and obsermined by the ratio of the peak intensity of the polymer to that of polymer plus monomer. The results of the study are shown in Table XIII.

#### TABLE XIII

_
Percent Conversion to Polymer from NMM Study

a MARY's taken on a 400 MHz instrument b Pigme detected in the MARY.

As can be seen from the NMR results, this typiem efficiently initiated beth openy and has radical polymentation simultaneously. Curing against comprising other combinations of organismstatic compounds and column satis can be used in piece of [CpFe(CO)s is and Mins(CO)s and Mins(Fig. respectively).

#### EXAMPLE 20

in a crossimilable system. The curable composition consists of methyl acrylate, cyclohesiene oside and polymer. Only if both epoxy and acrylate cure are initiated will a crosslinked insoluble polymer be glycodyl acrylete. If only epoxy or acrylete cure are imbated, then this system will produce a soluble This example demonstrates the simultaneous curing of ethylenically unsaturated and epoxy monomers

Semple preparations were carried out under subdued lights. The polymerizable musture consisted of 0.2.9. genma-bulynolectore. 1.0 g głycdył acrylae. 5.0 g methyl acrylae and 5.0 g cyclohexene oxide Depending on the test, added to this were 0.05 g of the desired organometalic compound and or 0.1 g sprenylodonum haushuorophosphase. A 3 g porson of this composition was placed in a glass vial and possed between two, 15 watt G.E. daylight fluorescent builds using an Ultraviolet Products lamp holder As monomers were distilled before use, methyl acrylate and glycidyl acrylate from hydroquinone

(temp separation distance 4 cm). The sample was purged with nitrogen for one minute preceeding and continuously during photolysis. The irradiation time required to produce a polymei insoluble in chloroform was recorded, and is noted in Table XIV. Alternatively, these compositions can be cured thermally.

#### TABLE XIV

[CpFe(COls): CpFe(COls):SnPhi CpFe(COls):SnPhi (CpFe(COls):SnPhi (Cpfe(COls):SnPhi (COls):MnSnPhi (COls):MnSnPhi (COls):MnSnPhi (Cols):MnSnPhi (Cols):MnSnPhi (Cols):MnSnPhi		Compound	Smultaneous Photombation of Free Radical and Epoxy Cure in a Crossinhable System
>15 >15 >15 >16 >16 >16 >16	No Onum San Added	Cure Time	apon of Free R rossimhable Sy
0 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 - 5 -	Added Added	26.	stem
		٠.	٠.

CoMo(CO): Solins a time in minutes to produce insoluble crossimked system b Only 0 019 of this compound used does not produce a crossimiled system after 15 minutes Dynamyhodonum hasaltuorophosphata alone under these conditions

sufficial departuring from the scope and spirit of this invention, and it should be understood that this invention Various moderations and attenuations of this evention will become apparent to those stilled in the art

A ACI ID IN LAGARY IN and to the divetable embodiments set forth herein

An energy solymerizable composition comprising

(2) at least one about stonor THE OF THE PARTY ct e crossé ades combinede and procureous pac compound, and

(2) as once as . 22

2. The composition according to claim 1 wherein said organometalist compound has the just

. L' represents none, or 1 to 12 ligands contributing prejections that can be the same  $\omega$  . substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds indiselected from substituted and unsubstituted acyclic and cyclic unsaturated compounds ar

contributing 2 to 24 prejections to the valence shell of M. sigma-electrons selected from monor, dir. and tri-densite equands, each donating 2. 4  $\times$  6  $\times$ L3 represents none, or 1 to 24 ligands that can be the same or different/contributing an in-

L3 represents none, or 1 to 12 igands that can be the same or different, each contribut-

one sigma-electron each to the valence shall of each M: M represents 1 to 4 of the same or different metal atoms selected from the elements .1 Ligands  $\mathbb{L}^1,\mathbb{L}^2$ , and  $\mathbb{L}^1$  can be bridging or non-bridging ligands.

. L1, and with the provise that  $L^{\prime},L^{2},L^{3},$  and M are chasen so as to achieve IVB, VB, VIB, VIB, and VIIIB. with the proviso that said organometalist compound contains at least one

wherein A is an iodonium, sulforium, or diazonium cabon, and 3 The composition according to claims 1 and 2 wherein said online said has the form

selected from the group consisting of acrylates, acrylamides and entyl compounds  $\chi$  is an organic suitonate counterion, or a halogenated metal or metalloid counterion of polyisocyanates and compounds bearing at least two isocyanate-reactive nyoroger of socyanate groups to isocyanate-reactive involvagen atoms is in the range 1.2 to 2.1  $\,$ 5. The composition according to claims it to 4 wherein said polywerhane procurs: 4. The composition according to claims 1 to 4 wherein said editrienically units

8. A process comprising the steps of 7. A layered structure comprising a substrate naving coated on one surface !! b) anowing said musture to polymerize or adding energy to said musture to energy a) providing a polymenizable minute according to claims 1 to 5 and

¥ composition according to claims 1 to 5 9. A shaped arbore comprising the composition according to claims 1 to 5. 8. The layered structure according to claim 7 enion is an imageable structure.

1). The composition according to claims 1 to 5 and 7 to 9 which has been  $\sim$ 

2. The composition according to claim 1 wherein said organometalist compound has the formula.

substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of L represents none; or 1 to 12 ligands contributing prefections that can be the same or different ligand selected from substituted and unsubstituted advotic and cyclic unsaturated compounds and groups and

sigms-esections selected from monor, dr., and midentate ligands, each donating 2: 4, or 6 sigms-electrons L<sup>2</sup> represents none, or 1 to 24 ligands that can be the same or different contributing an even number of

L<sup>3</sup> represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each Mil

 $L^3$  and with the proviso that  $L^1, L^2, L^3$ , and M are chosen so as to achieve a stable configuration. IVE VE VIE VIE and VIIIE. sen the proviso that said organometalist compound contains at least one of a metal-metal sigma bond and M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups 3. The composition according to claims 1 and 2 wherein said online sait has the formula II.

micronum a en te . 'e. poting and MEDICA THE L DOM WITH CORP. D.

ÇK Ö

اللائن المري , d 

arem A is an iodonium, suborium, or diazonium cabon, and i

It is an organic sudonate counterion, or a halogenated metal or metalloid counterion. 4. The composition according to claims 1 to 4 wherein said ethylenically-unsaturated monomer is

or polyrsocyanates and compounds bearing at least two isocyanate-reactive hydrogen atoms where the ratio of spocyanate groups to isocyanate-reactive hydrogen atoms is in the range 1.2 to 2.1 selected from the group consisting of acrylates, acrylamides and vinyl compounds. 5 The composition according to claims 1 to 4 wherein said polyurethane precursors comprise a mixture

6 A process comprising the steps of 7. A layered structure comprising a substrate having coated on one surface thereof the polymerizable b) allowing said musture to polymerize or adding energy to said musture to effect polymerization a) providing a polymerizable murture according to claims 1 to 5 and

composition according to claims 1 to 5. 8 The layered structure according to claim 7 which is an imageable structure

9 A shaped article comprising the composition according to claims 1 to 5 10. The composition according to claims 1 to 5 and 7 to 9 which has been cured

to sent it the an

or picks up no cotton threads  ${}^{\dagger} This$  test establishes the time required in conditions of this test, the appropriedonium heighborophosphate aurie (e.b.) in air, to a 275 wast GE suntains at a distance of 10cm. The time to "set 1.00 ii.) that is the time needed to cure the coating so that when it is touched with chloride subbed polyester (366 Company) using a #22 erre erund that The highling ded to prepare the costing solution. The solutions were costed units its institutions

TABLE V

		· .		_	
שיו ני בשוחתונו חי שתון	[CpFetCO):L CpFetCO): SnPn CpFetCO): GnPn (CpFetCO):L SnPn (CpFetCO):L Nn: (CO). Nn: (		Campound	Photomhabor	-
•	• - 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	No Onium Sat Acced	Cure Time	Photoinitation of Eposy July	
		Gnium Sa Austoit	10.		

EXAMPLE 11 .Comparative.

another epony and/or acrylate composition. The organishedalist coff-Diphenylodonum nezalkoróphosonale was recrystalitzed from a c obtained from Audrich. The organometalist compounds were acrylate was distribed from hydocumpyte and stored and until reedwas principled in presence of an epony or activate. The sce cone as 100% solids except as noted. To humber demonstrate the activity of the curing agent a Sr.

sec before and continuously during the photosysis. The econy test sair aung eith 2 g of the dealern munumer. For the attrible tests upon to the air The light soutce was one 15 well daily in a small vial was parted 0.02 g of the organizholaint com-

umes represent the time required to reach the same Americatively the actificate compositions can be cured their